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Chapter 16

Combustion, reactive hazard, and bioprocess safety

Chapter outline

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What is reactivity hazard? How to ensure safety? As we have learned in this text, the numerous chemical and biotransformations can be applied in industrial processes and in our daily practices. Transformation, as it sounds, involves changes. Any changes have irreversible consequences. Therefore, for a biotransformation process, either purely chemical or biological, safety is the key for its implementation. While danger of biological process can be long-lasting and unpredictable (or unknown), chemical processes can pose sudden dramatic impacts. Biological processes are thus highly regulated. Containment and quarantine have been the commonly accepted prevention method for biohazards. For example, the recent memory includes the Ebola outbreak in West Africa, Middle East respiratory syndrome (MERS), severe acute respiratory syndrome (SARS), Bovine spongiform encephalopathy (BSE). These outbreaks were first contained and then eradicated. Both chemical and biological hazards are extremely difficult to deal when they occur. Therefore, prevention of accidents from occurring is a paramount goal of design and operation of a process. The root causes of the process hazards can come from two sources—the first of which is the reagents or chemicals and the second of which is the structures. Operational safety lies on the industrial regulations. Bioprocess engineers are at the forefront of the industrial safety and a brief discussion is thus warranted in this chapter, in particular for the reagents and structures.

A significant aspect of bioprocess engineering is the consideration of possible accidents that could occur in biological and chemical processes in order to consider all possible modes by which the system can malfunction. We generally design a reactor system to give maximum yield of a desired product with the simplest and least-expensive equipment and the lowest-operating costs. This optimum design goal is evidently discussed on in a number of chapters in this text, for example, Chapters 3, 4, 5, 7, 13, 14, and 15. However, we also need to consider whether that design is also sufficiently robust that it will be stable for any unforeseen situations that may arise. The stability and sustainability of the reactor system of bioprocess

are important as discussed in Chapter 15. We need to consider operating modes outside of the regime of optimal design and determine that all possible situations in which the system may be operated will not lead to uncontrollable consequences. Chain reactions and/or uncontrolled combustion/explosion are often associated with accidents and thus we shall have a discussion on the combustion and their applications in industry as well.

16.1 Biological hazards

Biological agents or living organisms by nature pose hazards to other living organisms including human. For bioprocess engineers, microorganisms are commonly of concern, although macro-organisms such as animals, insects, and plants could be more common for agricultural biological engineers and biomedical engineers. In this chapter/section, we will limit our discussions on microorganisms. The relative hazards of infective microorganisms are classified by risk group as shown in Table 16.1, which is often used for laboratory work only.

In aligning with the four bio-risk groups, laboratory facilities are designated in meeting four biosafety levels as well. The four biosafety levels (BSL) as shown in Chapter 12 are—BSL 1 – basic; BSL 2 – basic; BSL 3 – containment; and BSL 4 – maximum containment. Biosafety level designations are based on a composite of the design features, construction, containment facilities, equipment, practices, and operational procedures required for working with agents from the various risk groups. Table 16.2 relates but does not “equate” risk groups to the biosafety level of laboratories designed to work with organisms in each risk group. Different countries (regions) draw up their own national (regional) classification of microorganisms, by risk group, taking into account:

1. Pathogenicity of the organism.

TABLE 16.1 Classification of infectious microorganisms by risk group

Risk group classification	NIH guidelines for research involving recombinant DNA molecules 2002	World Health Organization laboratory biosafety manual third edition 2004
Risk group 1	Agents not associated with disease in healthy adult humans.	(No or low individual and community risk) A microorganism unlikely to cause human or animal disease.
Risk group 2	Agents associated with human disease that is rarely serious and for which preventive or therapeutic interventions are often available.	(Moderate individual risk; low community risk) A pathogen that can cause human or animal disease but is unlikely to be a serious hazard to laboratory workers, the community, livestock or the environment. Laboratory exposures may cause serious infection, but effective treatment and preventive measures are available and the risk of spread of infection is limited.
Risk group 3	Agents associated with serious or lethal human disease for which preventive or therapeutic interventions may be available (high individual risk but low community risk).	(High individual risk; low community risk) A pathogen that usually causes serious human or animal disease but does not ordinarily spread from one infected individual to another. Effective treatment and preventive measures are available.
Risk group 4	Agents likely to cause serious or lethal human disease for which preventive or therapeutic interventions are not usually available (high individual risk and high community risk).	(High individual and community risk) A pathogen that usually causes serious human or animal disease and can be readily transmitted from one individual to another, directly or indirectly. Effective treatment and preventive measures are not usually available.

TABLE 16.2 Relation of risk groups to biosafety levels, practices and equipment.

Risk group	Biosafety level	Laboratory type	Laboratory practices	Safety equipment
1	BSL 1 – Basic	Basic teaching, research	good microbiological techniques (GMT)	None; open bench work
2	BSL 2 – Basic	Primary health services; diagnostic services, research	GMT plus protective clothing, biohazard sign	Open bench plus biological safety cabinet (BSC) for potential aerosols
3	BSL 3 – Containment	Special diagnostic services, research	As BSL 2 plus special clothing, controlled access, directional airflow	BSC and/or other primary devices for all activities
4	BSL 4 – Maximum containment	Dangerous pathogen units	As BSL 3 plus airlock entry, shower exit, special waste disposal	Class III BSC, or positive pressure suits in conjunction with Class II BSCs, double ended autoclave (through the wall), filtered air

2. Mode of transmission and host range of the organism. These may be influenced by existing levels of immunity in the local population, density, and movement of the host population, presence of appropriate vectors, and standards of environmental hygiene.
3. Local availability of effective preventive measures. These may include— prophylaxis by immunization or administration of antisera (passive immunization); sanitary measures, for example, food and water hygiene; control of animal reservoirs, or arthropod vectors.
4. Local availability of effective treatment. This includes passive immunization, postexposure vaccination, and use of antimicrobials, antivirals, and chemotherapeutic agents, and should take into consideration the possibility of the emergence of drug-resistant strains.

Biosafety is paramount to the public and potential of biohazard needs to be conveyed clearly to the personnel involved. [Fig. 16.1](#) shows the international warning sign of biohazard. Local languages are to be adopted to ensure the message can be understood. The assignment of an agent to a biosafety level for laboratory work must be based on a risk assessment. Such an assessment will take the risk group as well as other factors into consideration in establishing the appropriate biosafety level. For example, an agent that is assigned to Risk Group 2 may generally require Biosafety Level 2 facilities, equipment, practices, and procedures for safe conduct of work. However, if particular experiments require the generation of high-concentration aerosols, then Biosafety Level 3 may be more appropriate to provide the necessary degree of safety, since it ensures superior containment of aerosols in the laboratory workplace. The biosafety level assigned for the specific work to be done is therefore driven by professional judgment based on a risk assessment, rather than by automatic assignment of a laboratory biosafety level according to the particular risk group designation of the pathogenic agent to be used. [Table 16.3](#) summarizes the facility requirements at the four biosafety levels.

Thus, the assignment of a biosafety level takes into consideration the organism (pathogenic agent) used, the facilities available, and the equipment practices and procedures required conducting work safely in the laboratory.

The concept of Biological Safety (or biosafety) has paralleled the development of the science of microbiology and its extension into new and related areas including tissue culture, recombinant DNA, animal studies, molecular biology, synthetic biology, and biotechnology. The knowledge and skill gained by microbiologists necessary to isolate, manipulate, and propagate pathogenic microorganisms required parallel development of containment principles, facility design, and practices and procedures to prevent occupational infections in the workplace or release of the organisms to the environment.

Biosafety entails safe microbiological practices, procedures, and proper use of containment equipment and facilities. To be prudent in biosafety, one must develop knowledge of the principles of epidemiology, disease transmission patterns, risk-assessment and risk management, disinfection and sterilization, disease prevention, aerobiology and environmental control. The particular proficiencies a biosafety professional should possess as described by American Biological Safety Association (ABSA) include:

1. *Disinfection, decontamination, sterilization.* What is the difference between sterilization, decontamination, and disinfection? When and/or where to apply these eradication technique? How do you monitor their efficiency? How and where to use, and what are the potential hazards (explosive, flammable, corrosive, carcinogenic, and irritating) associ-



FIGURE 16.1 International biohazard warning sign for laboratory doors.

TABLE 16.3 Summary of biosafety level requirements.

	Biosafety level (BSL)			
	1	2	3	4
Isolation ^a of laboratory	No	No	Yes	Yes
Room sealable for decontamination	No	No	Yes	Yes
Ventilation: inward airflow	No	Desirable	Yes	Yes
controlled ventilating system	No	Desirable	Yes	Yes
HEPA ^b -filtered air exhaust	No	No	Yes/No ^c	Yes
Double-door entry	No	No	Yes	Yes
Airlock	No	No	No	Yes
Airlock with shower	No	No	No	Yes
Anteroom	No	No	Yes	-
Anteroom with shower	No	No	Yes/No ^d	No
Effluent treatment	No	No	Yes/No ^d	Yes
Autoclave: on site	No	Desirable	Yes	Yes
in laboratory room	No	No	Desirable	Yes
double-ended	No	No	Desirable	Yes
Biological safety cabinets	No	Desirable	Yes	Yes
Personnel safety monitoring capability ^e	No	No	Desirable	Yes

^aEnvironmental and functional isolation from general traffic.
^bHigh-efficiency particulate air;
^cnot recirculated to other areas within the building. Air may be high-efficiency particulate air (HEPA) filtered, reconditioned and recirculated within that laboratory.
^dDependent on agent(s) used in the laboratory.
^eFor example, window, closed-circuit television, two-way communication.

ated with various disinfectants and sterilants? How to use chemicals, steam, dry heat, irradiation, filtration, ultraviolet (UV) sources, gases, or other agents to kill or inactivate microorganisms?

2. *Work practices and procedures.* What are the good microbiological techniques, including sterile (aseptic) techniques? Understand the importance of developing, evaluating, and documenting exposure control procedures for biohazardous agents and materials. Develop procedures and practices to prevent release of infectious aerosols from equipment. Perform biosafety audit of work practices and procedures associated with large-scale operations. Understand and apply monitoring techniques and equipment to determine effectiveness of exposure control measures and to investigate environmental problems. Understand the use and disposal of sharps. Select and understand use of personal protective equipment. Select and understand use of respiratory equipment. Develop and implement procedures for managing biohazardous spills and releases. Assure documentation of worker exposure to biohazardous materials and preparation of an incident report. Develop comprehensive emergency response plan for biohazard areas.
3. *Risk assessment and hazard identification — infectious agents and recombinant DNA.* Understand personal risk factors associated with microbial exposure. Assess the risk of occupational exposure and infection associated with handling infectious agents. Must be familiar with routes of exposure, modes of transmission, and other criteria that determine the hazard category of a microorganism. Able to assess the risk to the community from various work environments where infectious agents or sensitizing materials may be present. Understand microbial toxins and their potential to cause work-related illness. Able to recognize the characteristics of bacteria, viruses, fungi, and parasites. Understand the hazard of exposure of service personnel to biological materials. Understand factors that may affect susceptibility, resistance, or consequences of infection. Understand the difference between risk of infection and consequences of infection. Understand the risk associated with biological aerosols in the workplace, such as ventilation, indoor air quality, recirculation, and cooling towers. Understand the risk associated with point source release of biological aerosols in the workplace, such as from homogenizers, cell sorters, centrifuges, fermenters, and lasers. Understand the risks associated with recombinant DNA technology. Know the unique biosafety conditions associated with naturally or experimentally infected animals, including nonhuman primates.
4. *Regulatory aspects, standards, and guidelines.* Interpret and apply the NIH guidelines for research involving recombinant DNA molecules. Interpret and apply OSHA Blood-borne pathogens standard. Interpret and apply guidelines that classify

biohazardous agents according to risk. Interpret and apply guidelines for preventing transmission of *Mycobacterium tuberculosis* in the workplace. Interpret and apply regulations for packing, labeling, and shipping of infectious materials, diagnostic specimens, and medical waste. Interpret and apply import and export requirements associated with biological materials. Interpret and apply regulations associated with animal pathogens. Interpret and apply guidelines associated with the large-scale use of microorganisms. Interpret and apply the NSF International Standard/ American National Standard on Class II laminar flow biohazard cabinetry (NSF/ANSI 49). Interpret and apply OSHA law, standards, and directives as they relate to biohazards. Interpret and apply guidelines and regulations relating to infectious and medical waste. Familiar with agencies, such as WHO, CDC, NIH, OSHA, AAALAC, DOT, IATA, ICAO, DOD, EPA, USDA, and FDA, and their role and relationship with biosafety. Interpret and apply the CDC-NIH Biosafety in Microbiological and Biomedical Laboratories document and other pertinent CDC publications. Interpret and apply select agent regulations.

5. *Program management and development.* Understand the role and function of an institutional biosafety committee. Prepare and maintain a biosafety manual. Review project proposals and advise on biosafety issues. Advise on occupational health programs for persons working with biological materials. Provide and interpret biosafety resource and reference information. Organize and implement institutional biosafety compliance programs and audit their effectiveness. Institute, evaluate, and document biosafety training. Identify biological agents and materials in your institution. Develop and implement an infectious and medical waste-management program. Provide technical information and advice on products impacting biological safety. Develop and recommend biosafety policies.
6. *Equipment operation and certification.* Understand the use and validation of a steam autoclave. Understand the use and certification of biological safety cabinets (BSCs). Demonstrate knowledge of Class I, II, and III BSC design features, applications, and functions. Understand the calibration and use of air-measuring instruments to verify the safe operation of biological-safety equipment. Understand the design, function, and efficiency of HEPA filters. Understand the limitations in the use of equipment, such as fume hoods and clean benches, for work with biohazardous materials. Understand the use and validation of sterilizers using ethylene oxide (ETO) and vaporized hydrogen peroxide. Understand the equipment and chemicals used for space decontamination. Understand the use and applicability of animal containment equipment.
7. *Facility design.* Understand the functions and indications for use of primary and secondary barriers. Understand the difference and appropriateness of facility design to balance the need for hazard containment, personal product, and environmental protection. Review architectural and engineering plans and advise on biosafety issues. Verify that facilities as built meet minimum biosafety design criteria.

Before leaving this topic of biohazard, we should emphasize that biohazards or more specifically hazards of biological organisms is relative slow and have varied standards in different countries. Containment is the first-line of defense in combating biohazards. While dealing with a specific threat, the methods are similar in dealing with reactive hazards as we will learn in the subsequent sections.


16.2 Identifying chemical reactivity hazards


While biohazards or more specifically hazards of biological organisms can be relative slow and have varied standards in different countries, chemicals hazardous to the living can be dramatic and sudden. While containment is the first-line of defense in combating biohazards, containment alone is not effective in the prevention of reactive hazards. No containment is perfect and breaching of barriers can occur and is what we term accidents. After fires and explosions, the major accident that can occur in chemical processing is the release of a chemical that is hazardous to humans. Recall that one of the green chemistry tenants is to eliminate or reduce the use of toxic chemicals in a process. Benign solvents, such as air, water, carbon dioxide, and low-volatility solvents, such as ionic liquids and molten salt, are preferred. Still, the products we seek or produce are also commonly harmful substances when improperly released. Air and water can become contaminated with chemicals that cause harm. These hazards can be acute (causing immediate and critical harm to people as in the Bhopal accident in India) or chronic (ground-water contamination which can require years and millions of dollars for cleanup).

16.2.1 Chemical hazard labeling

To avoid inappropriate handling as well emergency response to accidents, chemicals need to be properly labeled. Chemicals are labeled following standardized systems. However, different countries and/or agencies have different standards. For example, the Hazardous Materials Identification System (HMIS) is a numerical hazard rating that incorporates the use of labels with color developed by the American Coatings Association as a compliance aid for the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard. OSHA is an agency of the United States Department of Labor. Similarly, the fire diamond, created by the National Fire Protection Association (NFPA) is also a numerical hazard rating. HMIS and NFPA identifications are shown in [Table 16.4](#). The hazards are generally divided into three main categories—health, flammability, and physical. The labeling is visual and easy to be understood.

TABLE 16.4 Chemical reactivity hazard code comparison between HMIS and NFPA identifications.

Hazardous Materials Identification System (HMIS)			National Fire Protection Association (NFPA)		
<div> <div>Chemical Name</div> <div>HEALTH 0</div> <div>FLAMMABILITY 0</div> <div>PHYSICAL HAZARD 0</div> <div>PERSONAL PROTECTION 0</div> </div>					
Color	Code	Hazard	Color	Code	Hazard
Blue / health	0	No significant risk to health.	Health (blue)	0	Poses no health hazard, no precautions necessary and would offer no hazard beyond that of ordinary combustible materials (e.g. wood, paper)
	1	Irritation or minor reversible injury possible.		1	Exposure would cause irritation with only minor residual injury (e.g. acetone, sodium bromate)
	2	Temporary or minor injury may occur.		2	Intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury (e.g., diethyl ether, ammonium phosphate)
	3	Major injury likely unless prompt action is taken and medical treatment is given.		3	Short exposure could cause serious, temporary or moderate residual injury (e.g., chlorine, liquid hydrogen, carbon monoxide)
	4	Life-threatening, major or permanent damage may result from single or repeated overexposures (e.g., hydrogen cyanide)		4	Very short exposure could cause death or major residual injury (e.g., hydrogen cyanide, phosgene, methyl isocyanate, hydrofluoric acid)
Red / flammability	0	Materials that will not burn (e.g., Water)	Flammability (red)	0	Materials that will not burn under typical fire conditions (e.g., carbon tetrachloride), including intrinsically noncombustible materials such as concrete, stone and sand (Materials that will not burn in air when exposed to a temperature of [820°C (1500°F)] for a period of 5 minutes)
	1	Materials that must be preheated before ignition will occur. Includes liquids, solids and semi solids having a flash point above 200°F (93°C) (e.g., Canola oil)		1	Materials that require considerable preheating, under all ambient temperature conditions, before ignition and combustion can occur (e.g., mineral oil). Includes some finely divided suspended solids that do not require heating before ignition can occur. Flash point at or above 93°C (200°F).
	2	Materials which must be moderately heated or exposed to high ambient temperatures before ignition will occur. Includes liquids having a flash point at or above 100°F (38°C) but below 200°F (93°C) (e.g., Diesel fuel).		2	Must be moderately heated or exposed to relatively high ambient temperature before ignition can occur (e.g. diesel fuel) and multiple finely divided suspended solids that do not require heating before ignition can occur. Flash point between 38 and 93°C (100 and 200°F).
	3	Materials capable of ignition under almost all normal temperature conditions. Includes flammable liquids with flash points below 73°F (23°C) and boiling points above 100°F (38°C), as well as liquids with flash points between 73°F and 100°F.		3	Liquids and solids (including finely divided suspended solids) that can be ignited under almost all ambient temperature conditions (e.g., gasoline, acetone). Liquids having a flash point below 23°C (73°F) and having a boiling point at or above 38°C (100°F) or having a flash point between 23 and 38°C (73 and 100°F).
	4	Flammable gases, or very volatile flammable liquids with flash points below 73°F (23°C), and boiling points below 100°F (38°C). Materials may ignite spontaneously with air (e.g., Propane).		4	Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily (e.g., acetylene, propane, liquid hydrogen). Includes pyrophoric substances. Flash point below 23°C (73°F).

Orange/physical hazard	0	Materials that are normally stable, even under fire conditions, and will not react with water, polymerize, decompose, condense, or self-react. Nonexplosives.	Instability/reactivity (yellow or orange)	0	Normally stable, even under fire exposure conditions, and is not reactive with water (e.g., helium, N ₂)
	1	Materials that are normally stable but can become unstable (self-react) at high temperatures and pressures. Materials may react non-violently with water or undergo hazardous polymerization in the absence of inhibitors		1	Normally stable, but can become unstable at elevated temperatures and pressures (e.g., propene)
	2	Materials that are unstable and may undergo violent chemical changes at normal temperature and pressure with low risk for explosion. Materials may react violently with water or form peroxides upon exposure to air.		2	Undergoes violent chemical change at elevated temperatures and pressures, reacts violently with water, or may form explosive mixtures with water (e.g., white phosphorus, potassium, sodium)
	3	Materials that may form explosive mixtures with water and are capable of detonation or explosive reaction in the presence of a strong initiating source. Materials may polymerize, decompose, self-react, or undergo other chemical change at normal temperature and pressure with moderate risk of explosion.		3	Capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked (e.g., ammonium nitrate, chlorine trifluoride)
	4	Materials those are readily capable of explosive water reaction, detonation or explosive decomposition, polymerization, or self-reaction at normal temperature and pressure.		4	Readily capable of detonation or explosive decomposition at normal temperatures and pressures (e.g., nitroglycerin, chlorine azide, chlorine dioxide)
White/personal protection	This is by far the largest area of difference between the NFPA and HMIS systems. In the NFPA system, the white area is used to convey special hazards whereas HMIS uses the white section to indicate what personal protective equipment (PPE) should be used when working with the material.		Special notice (white)	ALK	Alkaline
				ACID	Acidic
				OX	Oxidizer, allows chemicals to burn without an air supply (e.g., potassium perchlorate, ammonium nitrate, hydrogen peroxide).
					Radioactive
				W	Reacts with water in an unusual or dangerous manner (e.g., cesium, sodium, sulfuric acid).
				SA	Simple asphyxiant gas. Specifically limited to the following gases: nitrogen, helium, neon, argon, krypton, and xenon.


<p style="text-align: center;">OXI252 (disodiumflammy) CAS #: 111-11-18x</p> <div style="text-align: center;">  </div> <p style="text-align: center;">Danger</p> <p style="text-align: center;">May cause fire or explosion; strong oxidizer Causes severe skin burns and eye damage</p> <p>Keep away from heat. Keep away from clothing and other combustible materials. Take any precaution to avoid mixing with combustibles. Wear protective neoprene gloves, safety goggles and face shield with chin guard. Wear fire/flame resistant clothing. Do not breathe dust or mists. Wash arms, hands and face thoroughly after handling. Store locked up. Dispose of contents and container in accordance with local, state and federal regulations.</p> <p>First aid: IF ON SKIN (or hair) or clothing: Rinse immediately contaminated clothing and skin with plenty of water before removing clothes. Wash contaminated clothing before reuse. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. IF INHALED: Remove person to fresh air and keep comfortable for breathing. IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. Immediately call poison center. Specific Treatment: Treat with doctor-prescribed burn cream.</p> <p>Fire: In case of fire: Use water spray. In case of major fire and large quantities: Evacuate area. Fight fire remotely due to the risk of explosion.</p> <p>GHS ChemCo, 55 Main Street, Town, NY 13210 Telephone (888) 777-8888</p>	<p>Substance CAS number</p> <p>Pictogram(s)</p> <p>Single word Hazard Statements</p> <p>Precautionary Statements Prevention:</p> <p>Response:</p> <p>Specific Treatment</p> <p>In case of fire:</p> <p>Manufacture</p>
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FIGURE 16.2 Chemical labeling as issued by OSHA complies with GHS system (on the left) and the information identified (on the right).

While there are differences among different agencies and countries, the general messages are similar. To avoid confusion and promote trade, United Nations has created a universal identification system, global harmonized system of classification and labeling of chemicals (GHS), beginning in 1992. Fig. 16.2 shows a sample GHS chemical label. The GHS label includes the substance name, id, and eye-catching pictograms to show the potential dangers, warnings, and descriptions on how to handle it. Table 16.5 shows the pictograms of the different hazard classes. As shown in Table 16.5 the GHS hazard classification also includes three categories—Physical, health, and environment. As compared with HMIS and NPFA labeling, GHS combined the flammability hazards into physical hazard category while one additional category is added—environmental hazard.

The adoption of the GHS is expected to facilitate international trade by increasing consistency between the laws in different countries (and jurisdictions) that currently have different hazard communication requirements. There is no set international implementation schedule for the GHS. United States of America published the final rule for implementation of GHS on March 26, 2012. It required product manufacturers to adopt the standard by June 1, 2015; product distributors to adopt the standard by December 1, 2015, while workers had to be trained by December 1, 2013.

The physical hazards are assigned to 9 different hazard classes largely based on the United Nations Dangerous Goods System. These include:

1. *Explosives*, which are assigned to one of six subcategories depending on the type of hazard they present, as used in the UN Dangerous Goods System.
2. *Gases* are category 1 flammable if they start to flame in a range in air at 20°C and a standard pressure of 101.3 kPa. Category 2 are non-flammable and non-toxic gases, and category 3 are toxic gases. Substances and mixtures of this hazard class are assigned to one of two hazard categories on the basis of the outcome of the test or calculation method.
3. A *flammable liquid* is a liquid with a flash point of not more than 93°C. Substances and mixtures of this hazard class are assigned to one of four hazard categories on the basis of the flash point and boiling point. A pyrophoric liquid is a liquid that, even in small quantities, is liable to ignite within 5 minutes after coming into contact with air. Substances and mixtures of this hazard class are assigned to a single-hazard category on the basis of the outcome of the UN Test N.3.
4. A *flammable solid* is one that is readily combustible or may cause or contribute to fire through friction. Readily combustible solids are powdered, granular, or pasty substances which are dangerous if they can be easily ignited

TABLE 16.5 Globally harmonized system of classification and labeling of chemicals (GHS).

Physical hazards	Health hazards	Environmental hazards
Explosive  Unstable explosives Explosives, divisions 1.1, 1.2, 1.3, 1.4 Self-reactive substances and mixtures, types A, B Organic peroxides, types A, B	Toxic  Acute toxicity (oral, dermal, inhalation), categories 1, 2, 3	Environmental hazard  Acute hazards to the aquatic environment, category 1 Chronic hazards to the aquatic environment, categories 1, 2
Flammable  Flammable gases, category 1 Flammable aerosols, categories 1, 2 Flammable liquids, categories 1, 2, 3 Flammable solids, categories 1, 2 Self-reactive substances and mixtures, types B, C, D, E, F Pyrophoric liquids, category 1 Pyrophoric solids, category 1 Self-heating substances and mixtures, categories 1, 2 Substances and mixtures, which in contact with water, emit flammable gases, categories 1, 2, 3 Organic peroxides, types B, C, D, E, F	Harmful  Acute toxicity (oral, dermal, inhalation), category 4 Skin irritation, categories 2, 3 Eye irritation, category 2A Skin sensitization, category 1 Specific target organ toxicity following single exposure, category 3 Respiratory tract irritation Narcotic effects	
Oxidizing  Oxidizing gases, category 1 Oxidizing liquids, categories 1, 2, 3 Oxidizing solids, categories 1, 2, 3	Corrosive  Skin corrosion, categories 1A, 1B, 1C Serious eye damage, category 1	
Cylinder  Compressed gases Liquefied gases Refrigerated liquefied gases Dissolved gases	Health hazard  Respiratory sensitization, category 1 Germ cell mutagenicity, categories 1A, 1B, 2 Carcinogenicity, categories 1A, 1B, 2 Reproductive toxicity, categories 1A, 1B, 2 Specific target organ toxicity following single exposure, categories 1, 2 Specific target organ toxicity following repeated exposure, categories 1, 2 Aspiration hazard, categories 1, 2	
Corrosive  Corrosive to metals		

Source: Based on Globally Harmonized System of Classification and Labeling of Chemicals (Second revised ed.), New York and Geneva: United Nations, 2007, ISBN 978-92-1-116957-7, ST/SG/AC.10/30/Rev.2 ("GHS Rev.2")

by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly. It is further divided into

- a. flammable solids,
 - b. polymerizing substances and
 - c. self-reactive substances, that is, thermally unstable solids liable to undergo a strongly exothermic thermal decomposition even without participation of oxygen (air) other than materials classified as explosive, organic peroxides, or as oxidizing agents. Spontaneously combusting solids or pyrophoric solids are solids that, even in small quantities, are liable to ignite within 5 minutes after coming into contact with air. Substances and mixtures of this hazard class are assigned to a single-hazard category on the basis of the outcome of the UN Test N.2. Self-heating substances are solids or liquids, other than a pyrophoric substance, which, by reaction with air and without heat supply, is liable to self-heat. Substances and mixtures of this hazard class are assigned to one of two hazard categories on the basis of the outcome of the UN Test N.4. Substances which on contact with water emit flammable gases are liable to become spontaneously flammable or to give-off flammable gases in dangerous quantities. Substances and mixtures of this hazard class are assigned to one of three hazard categories on the basis of the outcome of UN Test N.5, which measures gas evolution and speed of evolution. Flammable aerosols can be classified as Class 1 or Class 2 if they contain any component, which is classified as flammable.
5. *Oxidizing substances and organic peroxides* contain category 1 oxidizing substances and category 2 organic peroxides, organic liquids or solids that contain the bivalent -O-O- structure and may be considered a derivative of hydrogen peroxide, where one or both of the hydrogen atoms have been replaced by organic radicals. The term also includes organic peroxide formulations (mixtures). Substances and mixtures of this hazard class are assigned to one of seven "Types," A to G, on the basis of the outcome of the UN Test Series A to H.
 6. *Toxic and infectious substances*
 7. *Radioactive substances*
 8. *Substances corrosive to metal* are substances or mixtures that by chemical action will materially damage, or even destroy metals. These substances or mixtures are classified in a single hazard category on the basis of tests (Steel: ISO 9328 (II): 1991 - Steel type P235; Aluminum: ASTM G31-72 (1990) - non-clad types 7075-T6 or AZ5GU-T66). The GHS criteria are a corrosion rate on steel or aluminum surfaces exceeding 6.25 mm per year at a test temperature of 55°C.
 9. *Miscellaneous dangerous substances* which includes environmentally dangerous substances.

The health hazards are classified based on 12 areas. These include:

- *Acute toxicity* includes five GHS categories from which the appropriate elements relevant to transport, consumer, worker and environment protection can be selected. Substances are assigned to one of the five toxicity categories on the basis of LD₅₀ (oral, dermal) or LC₅₀ (inhalation).
- *Skin corrosion* means the production of irreversible damage to the skin following the application of a test substance for up to 4 hours. Substances and mixtures in this hazard class are assigned to a single harmonized corrosion category.
- *Skin irritation* means the production of reversible damage to the skin following the application of a test substance for up to 4 hours. Substances and mixtures in this hazard class are assigned to a single irritant category. For those authorities, such as pesticide regulators, wanting more than one designation for skin irritation, an additional mild-irritant category is provided.
- *Serious eye damage* means the production of tissue damage in the eye, or serious physical decay of vision, following application of a test substance to the front surface of the eye, which is not fully reversible within 21 days of application. Substances and mixtures in this hazard class are assigned to a single-harmonized category.
- *Eye irritation* means changes in the eye following the application of a test substance to the front surface of the eye, which are fully reversible within 21 days of application. Substances and mixtures in this hazard class are assigned to a single harmonized hazard category. For authorities, such as pesticide regulators, wanting more than one designation for eye irritation, one of two subcategories can be selected, depending on whether the effects are reversible in 21 or 7 days.
- *Respiratory sensitizer* means a substance that induces hypersensitivity of the airways following inhalation of the substance. Substances and mixtures in this hazard class are assigned to one hazard category.
- *Skin sensitizer* means a substance that will induce an allergic response following skin contact. The definition for "skin sensitizer" is equivalent to "contact sensitizer." Substances and mixtures in this hazard class are assigned to one hazard category.
- *Germ cell mutagenicity* means an agent giving rise to an increased occurrence of mutations in populations of cells and/or organisms. Substances and mixtures in this hazard class are assigned to one of two hazard categories. Category 1 has two subcategories.
- *Carcinogenicity* means a chemical substance or a mixture of chemical substances that induce cancer or increase its incidence. Substances and mixtures in this hazard class are assigned to one of two hazard categories. Category 1 has two subcategories.

- *Reproductive toxicity* includes adverse effects on sexual function and fertility in adult males and females, as well as developmental toxicity in offspring. Substances and mixtures with reproductive and/or developmental effects are assigned to one of two hazard categories, “known or presumed” and “suspected.” Category 1 has two subcategories for reproductive and developmental effects. Materials, which cause concern for the health of breastfed children, have a separate category, Effects on or Via Lactation.
- *Specific target organ toxicity (STOT)* category distinguishes between single and repeated exposure for target-organ effects. All significant health effects, not otherwise specifically included in the GHS, that can impair function, both reversible and irreversible, immediate and/or delayed are included in the nonlethal target organ/systemic toxicity class (TOST). Narcotic effects and respiratory tract irritation are considered to be target organ-systemic effects following a single exposure. Substances and mixtures of the single exposure target organ toxicity hazard class are assigned to one of three hazard categories. Substances and mixtures of the repeated exposure target organ toxicity hazard class are assigned to one of two-hazard categories.
- *Aspiration hazard* includes severe acute effects such as chemical pneumonia, varying degrees of pulmonary injury or death following aspiration. Aspiration is the entry of a liquid or solid directly through the oral or nasal cavity, or indirectly from vomiting, into the trachea and lower-respiratory system. Substances and mixtures of this hazard class are assigned to one of two hazard categories this hazard class on the basis of viscosity.

And the environmental hazards are classified in two areas:

- *Acute aquatic toxicity* means the intrinsic property of a material to cause injury to an aquatic organism in a short-term exposure. Substances and mixtures of this hazard class are assigned to one of three toxicity categories on the basis of acute toxicity data: LC₅₀ (fish) or EC₅₀ (crustacean) or ErC₅₀ (for algae or other aquatic plants). In some regulatory systems these acute toxicity categories may be subdivided or extended for certain sectors.
- *Chronic aquatic toxicity* means the potential or actual properties of a material to cause adverse effects to aquatic organisms during exposures that are determined in relation to the lifecycle of the organism. Substances and mixtures in this hazard class are assigned to one of four toxicity categories on the basis of acute data and environmental fate data—LC₅₀ (fish) or EC₅₀ (crustacea) or ErC₅₀ (for algae or other aquatic plants) and degradation or bioaccumulation.

Besides the chemical labeling, detailed data must be provided for safe-handling of the particular chemical. The safety data sheet (SDS, formerly known as material safety data sheet or MSDS) is specifically aimed at use in the workplace. It provides comprehensive information about the chemical product that allows employers and workers to obtain concise, relevant, and accurate information that can be put in perspective with regard to the hazards, uses, and risk management of the chemical product in the workplace. The SDS contains 16 sections. While there are some differences in existing industry recommendations, and requirements of countries, there is widespread agreement on a 16 section SDS that includes the following headings in the order specified:

1. Identification
2. Hazard(s) identification
3. Composition/information on ingredients
4. First-aid measures
5. Fire-fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure control/ personal protection
9. Physical and chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information
16. Other information.

The GHS SDS headings, sequence, and content are similar to the ISO, EU and ANSI MSDS/SDS requirements. The SDS provides a clear description of the data used to identify the hazards.

16.2.2 Chemical reactivity hazard

The current industry consensus defines chemical reactivity hazard as a situation where an uncontrolled chemical reaction could result directly or indirectly in serious harm to people, property, or the environment.

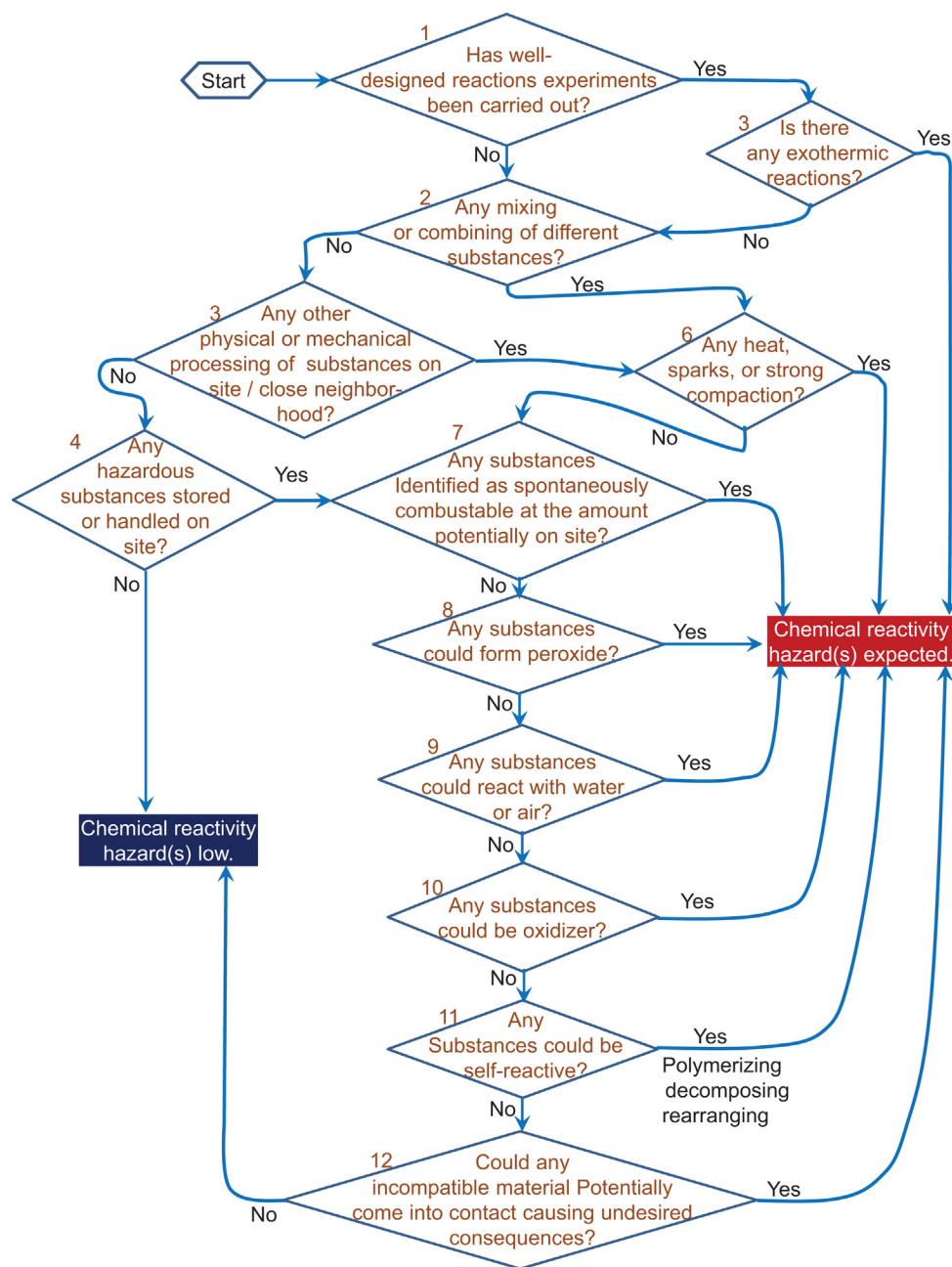


FIGURE 16.3 A summary of prescreening questions for chemical reactivity hazards.

The Environmental Protection Agency (EPA) issued an Alert in 2004 [EPA 550-F-04-004 (5104A) www.epa.gov/ceppo] as part of its ongoing effort to protect human health and the environment by preventing chemical accidents. EPA is striving to learn the causes and contributing factors associated with chemical accidents and to prevent their recurrence. Major chemical accidents cannot be prevented solely through regulatory requirements. Rather, understanding the fundamental root causes, widely disseminating the lessons learned, and integrating these lessons learned into safe operations are also required. EPA publishes Alerts to increase awareness of possible hazards. It is important to review this information and consider whether additional action is needed to address the hazards. The purpose of this Alert is to introduce small- and medium-sized facilities to a simple method developed by the Center for Chemical Process Safety (CCPS), essential practices for managing chemical reactivity hazards, to screen facilities for chemical reactivity hazards. The CCPS preliminary screening method as illustrated in Fig. 16.3 is a tool to help one identify where chemical reactivity hazards are likely to occur in a facility and may be applicable to a wide range of activities including warehousing, repackaging, blending, mixing, and processing.

TABLE 16.6 shows the typical causes of reactivity incidents.

Self-reacting chemicals

- Improper change of temperature (either heat / cold)
- Mechanic contact (mechanic shock, impact or impingement, friction)
- Spark
- Exposure to light
- Presence of contaminant(s)
- Loss, absence, or inactivation of stabilizer, inhibitor, or diluent
- High concentration / large amount
- Excessive shelf time

Runaway reactions

- Insufficient, delayed, lost, or excessive heating, cooling, mixing, agitation, etc.
- Amounts, rates, or ratios of addition of reactants or catalysts are excessive or inadequate
- Incorrect reactants or catalysts charged
- Catalyst added at wrong time / sequence
- Presence of contaminants, including air or water
- Ingress of materials
- Reactants or catalysts that are too hot or too cold, incorrectly specified or added
- Side reactions (neglected or unaware)
- Incorrect sequence of addition of chemicals
- Incorrect or loss of control of process parameters and conditions (pH, level, vacuum, venting, etc.)
- Process steps performed too soon, too late, out of sequence, or omitted.

Reaction with process materials

- Presence of incompatible materials, e.g., lubricants, sealants, packing, utility fluids, materials of construction, rust, etc.
- Ingress of materials such as water, air, and utility fluids through containment penetrations or leaks
- Exposure of process chemicals to the atmosphere (moisture, oxygen, etc.)
- Absence or inactivation antioxidant or other stabilizers

Inadvertent mixing of process chemicals

- Incorrect chemicals delivered
- Incorrect chemicals charged
- Chemicals loaded or transferred to wrong vessels
- Breached containment

Many materials used in industrial facilities can pose chemical reactivity hazards. Reactivity hazards may not be as easy to identify as other hazards such as toxicity or corrosivity. A facility is at a higher risk of having an uncontrolled release if not all the existing chemical reactivity hazards are identified.

Table 16.6 shows the typical causes of reactivity incidents. One can infer that chemical reactivity hazards can be categorized as follows:

1. Self-reacting or unstable chemicals. A single-unstable compound can undergo uncontrolled decomposition, rearrangement, or polymerization. For example, organic peroxides can pose fire and explosion hazards.
2. Runaway reactions. Intended reactions of chemicals to produce desired products can become uncontrollable. For example, the reaction of phenol with formaldehyde to produce phenolic resins is subjected runaway.
3. Incompatibilities. Inadvertent mixing of two or more process chemicals may lead to an unintended chemical reaction. For example, mixing acids with cyanide salts generates highly toxic hydrogen cyanide gas, and mixing silver salts with ammonia in the presence of a strong base may generate an explosively unstable solid. Also, process chemicals may react with materials present in the process such as water, air, materials of construction, lubricating oils, utility fluids, etc. For example, acetylene reacts with copper to form explosive compounds, and phosgene reacts corrosively with stainless steel, which may result in loss of containment.

Most chemical reactions release heat, and many reactivity incidents involve the sudden release of heat in quantities or at rates too high to be absorbed by the immediate soundings. Potential consequences or reactivity incidents include

1. Overpressurization and rupture of closed containers and vessels, which can result in an explosion and projectiles that can cause injuries and property damage and/or the dispersal of hazardous materials and toxic exposures, fires, and violent explosions;
2. Generation of gases (toxic or combustive) or other hazardous materials (e.g., the generation of hydrogen sulfide by the inadvertent mixing of an acid with a sulfide solution);

3. Generation of heat that causes thermal burns and ignition of combustible materials;
4. Fire in the absence of an additional ignition source;
5. Initiation of other chemical reactions.

In order to avoid or manage the chemical reactivity hazard, the first step in managing chemical reactivity hazards is identifying those facility operations and chemicals that represent a potential chemical reactivity hazard. Fig. 16.3 shows a schematic flow diagram of steps to follow in identifying chemical reactivity hazards in a given facility. The screening method is based on a series of twelve “yes-or-no” questions to help one determine, if there are chemical reactivity hazards in the facility. Once the chemical reactivity hazards are identified in the facility, a hazard management system can be set-up to properly address them. Regulatory process safety and risk management systems such as the OSHA Process Safety Management Standard, and EPA’s Risk Management Program (RMP) incorporate elements that are applicable to the management of reactive chemicals and can be used as a basis. EPA believes that facilities have a general duty to address significant reactive chemical hazards under the general duty clause of section 112(r)(1) of the Clean Air Act.

A first step in accident prevention is to examine how the reactor performs under all possible feed conditions. What are the possible ranges of pressure, temperature, feed rate, feed compositions, and other variables that the system may possibly experience, and what will be their responses in the reactor and effluent? The bioprocess engineer needs to continuously be aware of these upsets or drifting away from the desired set point(s).

Efficient handling of upsets requires the knowledge of steady-state and transient behaviors of the reactor system. We have only discussed steady-state behavior except for (1) brief considerations in Chapters 4, 11, 12, 15, and (2) feed and thermal transients in CSTRs in Chapter 15. Numerical tools, such as ODEXLIMS, are useful in aiding the analysis.

It is important to build a model of the bioprocess early in process design and use this model to simulate all possible upsets. The bulk of this text deals with the kinetics or kinetic model of chemical and biotransformations, and thus there is no excuse not to be able to establish a reasonable mathematical model for the process under concern. After each possible upset has been examined individually, combinations of upsets need to be considered. What would happen when pressure, temperature, and feed substrate concentration suddenly rise at the same time?

16.3 Heat, flames, fires, and explosions

Fires and explosions are involved in most industrial accidents. Later in this Chapter we will examine some of the issues involved in flames, fires, and explosions, and these are some of the major issues that need consideration in accident prevention. Where are the most likely trouble spots and what are the consequences of an incident?

Heat, fire, explosion, and pressure generation are all features of undesired reactions. Reactive chemicals and materials, monomers, resins, peroxides, application interface’s batteries and explosives—all have the potential to produce heat by exothermic reactions, these typically are unwanted. If the heat is not removed there is the potential for a runaway reaction. There is the need to understand the likelihood and to assess the impact of “undesired reactions.” This can be done in the laboratory on a smaller scale with the aim to simulate the scenario of what can happen in real life on any larger industrial scale. Such an understanding of heat release from chemical reactions and the potential for runaway reactions is vitally important in many branches of the chemical & allied industries. When the heat generated by a chemical process is greater than the possible heat removal, the temperature will rise with perhaps catastrophic effect! An example will be shown at the end of the Chapter to illustrate importance of heat removal. Now, you are equipped with the ability to conduct detailed reactor analysis that can simulate such unknown exothermic runaway reactions, mimicking what can happen on large scale and giving worst-case data; data obtained under zero-heat loss conditions. What happens if a chemical or system self heats? Initially (near onset of self-heating) this reaction will be slow. In chemicals this gives a loss of yield, a shelf life issue. At this stage heat loss is likely to pose little potential of a runaway and an explosion. However should the reaction accumulate heat it will accelerate and as temperature raises the rate of reaction will also increase. If the reaction is not kept under control, a safety problem will occur, which may result in explosion, loss of property, even human injury or death. It is necessary to remove this heat of reaction to control the reaction. To maintain control of the reaction the heat loss must be greater than the heat production.

Fig. 16.4 shows a schematic of a simple-reactor system. Heat-exchanging capability is illustrated with jacket having a “cooling” (or “heating”) fluid passing through. If the reaction mixture volume is constant, we obtain from the first-law of thermodynamics [see Eq. (3.134)] similar to that in Chapter 15,

$$\sum_{j=1}^{N_s} Q C_{j0} (H_j - H_{j0}) + V r \Delta H_R + \sum_{j=1}^{N_s} V C_{pj} C_j \frac{dT}{dt} = \dot{Q} - \dot{W}_s \quad (16.1)$$

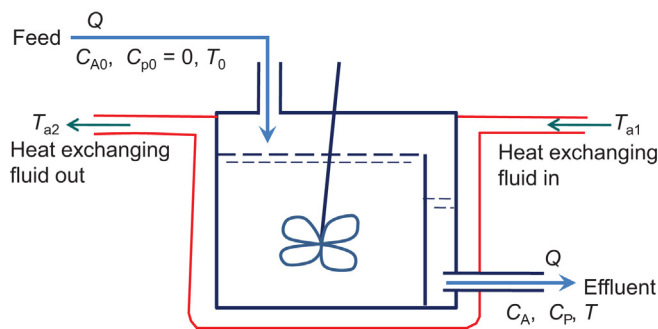


FIGURE 16.4 A jacketed reactor with heat-exchanging capacities.

The energy of stirring is dissipated into the reaction mixture, $\dot{W}_s \leq 0$. Heat transfer into the reactor is accomplished by the jacket:

$$\dot{Q} = UA_H (T_a - T)_m \quad (16.2)$$

where $(T_a - T)_m$ is the mean heat transfer temperature difference. Normally, log mean temperature difference is used.

$$(T_a - T)_m = \frac{T_{a2} - T_{a1}}{\ln \frac{T_{a2} - T}{T_{a1} - T}} \approx \frac{T_{a1} - T}{2} + \frac{T_{a2} - T}{2} \quad (16.3)$$

Assuming that the heat capacities are constant, we have

$$H_j - H_{j0} = C_{pj} (T - T_0) \quad (16.4)$$

Letting heat removal

$$H_R = \frac{Q}{V} \sum_{j=1}^{N_s} C_{j0} C_{pj} (T - T_0) - \frac{UA_H (T_a - T)_m - \dot{W}_s}{V} \quad (16.5)$$

and the heat generation

$$H_G = r(-\Delta H_R) \quad (16.6)$$

Eq. (16.1) can be reduced to

$$\frac{dT}{dt} = \frac{H_G - H_R}{\sum_{j=1}^{N_s} C_j C_{pj}} \quad (16.7)$$

The temperature will rise if the heat removal is not sufficient (as compared with the heat generation). At steady state,

$$H_R = H_G \quad (16.8)$$

As the rate of reaction r increases with temperature exponentially (Arrhenius law), Eq. (16.6) predicts that the heat produced will increase exponentially with temperature. However, the heat loss from vessel will only increase linearly with temperature as predicted by Eq. (16.5).

Scales of reaction and/or amounts of individual chemicals are different in R&D process development, manufacturing plants and transportation storage sites. The difference in the amount of chemicals poses different level of dangers. A small amount of any chemical may not be of acute danger to humans and environment, whereas large amount of any chemical can cause significant harm. The 2015 explosion in the port city of Tianjin, China, for example, shows that improper storage of chemicals (in this case nitrocellulose, and ammonium nitrate) can cause extreme harm. Over one hundred lives lost in the

explosion. For all potential runaway reactions, heat loss possibility and environmental conditions are important. Therefore, scale is important. A small vessel will lose more heat than a large vessel due to the available heat transfer area per volume of the reaction mixture; the large vessel is more adiabatic. A reactive material in a smaller vessel will be stable to a higher temperature than the same material in a larger vessel. The same sample may be safe in a beaker or drum – but may runaway in a tanker causing explosion. A battery may be stable as a single unit – but as a battery pack in a black cased Notebook alongside heat-producing electronic components heat output may raise the battery temperature causing disintegration and fire. To simulate the real-life or large-scale scenario, the sample under investigation must be in an environment without heat loss (or gain). The temperature where the heat production exceeds the heat loss is the temperature of no return (TNR). There is not just one TNR, this value will change as heat-loss potential changes. Vary the environment and the TNR can be reduced significantly.

16.4 Probabilities, redundancy, and worst-case scenarios

There is a continuing extensive literature on accidents and loss prevention in the chemical industry. This involves extensive use of statistics and probabilities in assessing damage and probable outcomes which are beyond what can be covered in this text. Chemical engineering progress runs a section of process safety each issue; the readers are encouraged to keep refreshing up. Safety consideration is a life-long learning issues that needing update as we understand more.

It is paramount to design a chemical process plant with sufficient redundancy able to respond to fluctuations that may occur. As a primary issue in reactor design is minimization of costs, any redundancy will clearly add cost and complexity to the process. Design with transients and accidents in mind are clearly an extremely complex subject that requires careful analysis and consultation before deciding on a final design of a process.

It is also important to determine the possible outcomes that could arise if the worst possible sequence of events should occur. Hurricanes can be accounted for and responded to as weather forecast is generally able to predict their occurrences. However, earthquakes and tornadoes are more difficult because there are no reliable forecasts available early enough to implement a procedure to shut-down the plant. Sabotage and intentional damage caused by insiders are very difficult to factor in because they require a response to conscious damage by people who are potentially well qualified to understand the maximum damage that could occur. How should one respond to a terrorist attack or a deliberate bombing act?

Fig. 16.5 shows one of the most spectacular chemical plant accidents ever. It occurred at an ammonium nitrate (fertilizer) factory in Ludwigshafen, Germany, on September 21, 1921. The blast dug a large crater of 90 m × 125 m with a depth of 19 m (which filled with water) and destroyed all buildings in the area. Everything within approximately half a mile of the blast was destroyed. It killed 500–600 people and injured 2000 more. More recent fertilizer plant accidents include the West Fertilizer Co., Texas, in 2013, and Toulouse, France in 2001.

16.5 Chain reactions

The concepts of chain reactions have been discussed in Chapter 6. Free-radical reactions, polymerization, and depolymerization/hydrolysis are examples of chain reactions as depicted in Chapters 6 and 8. If one recalls, the essence of these reactions are their three characteristic steps— (1) initiation, (2) propagation, and (3) termination. Combustion processes are fast and exothermic reactions that proceed by free-radical chain reactions. Combustion processes release large amounts of heat, and they have many applications in the production of power and heat, in incineration, automobiles, and even in rockets.

These processes combine many of the complexities of the earlier chapters—complex kinetics, mass transfer control, and large-temperature variations. They also frequently involve multiple phases because the oxidant is usually air while fuels are frequently liquids or solids such as coal, wood, and oil drops.

In addition to the importance of combustion reactors in chemical processes, uncontrolled combustion reactions create the greatest potential safety hazard in nature and the chemical industry. Therefore, all bioprocess engineers need to understand the basic principles of combustion reactors to recognize the need for their proper management and to see how improper management of combustion can cause unacceptable disasters.

We have introduced chain reaction in Chapter 6, Section 6.4, with a classic example of the decomposition of acetaldehyde to methane and carbon monoxide, Eq. (6.59). In this chapter, we choose another example, the decomposition of diethyl ether.



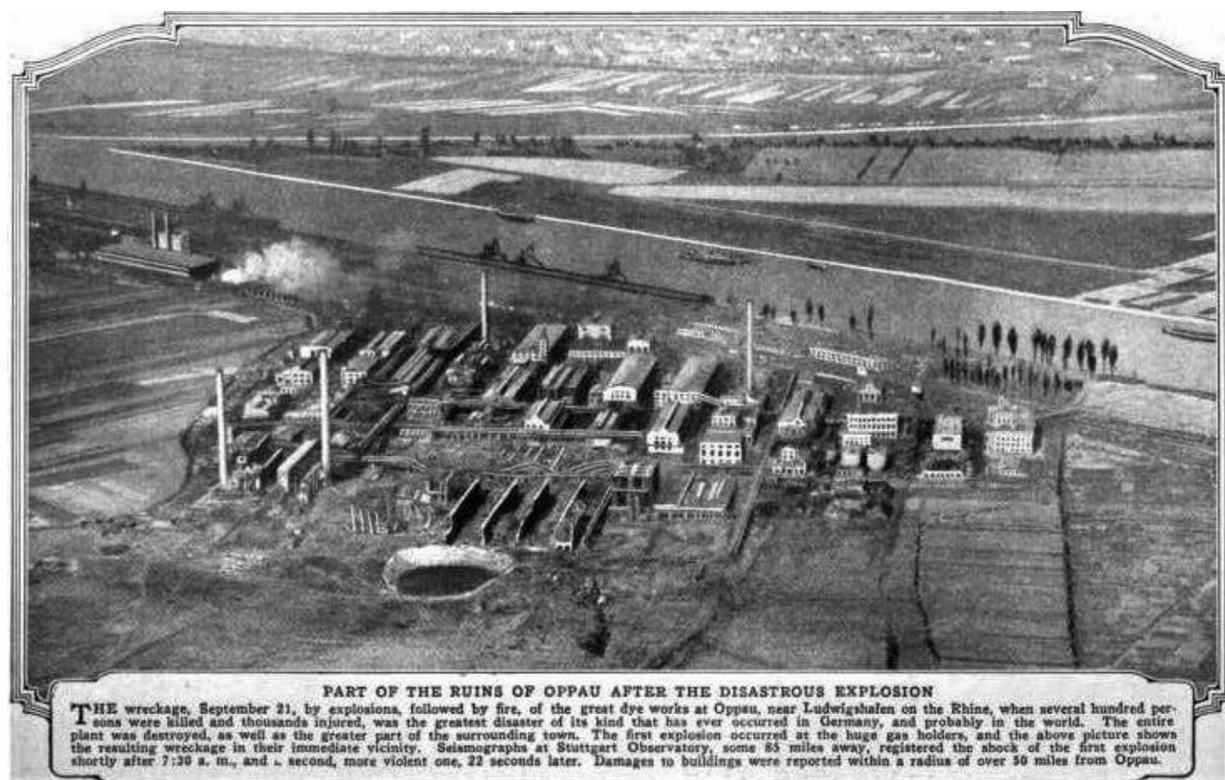
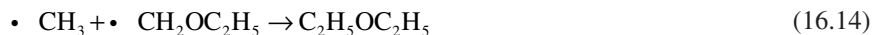
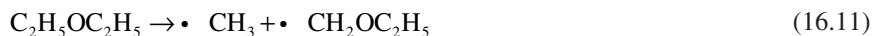


FIGURE 16.5 A BASF ammonium nitrate chemical plant following a massive explosion in 1921. You would not have wanted to be in charge of this plant or be anywhere near it when it blew up.

This reaction has an apparent rate expression of

$$r = k[\text{C}_2\text{H}_5\text{OC}_2\text{H}_5] \quad (16.10)$$

One may mistake the reaction as “elementary” as the rate law “agrees” with the stoichiometry. However, the reaction is in fact a complex reaction with free radicals. This is indeed a simple chain reaction, and it is a prototype of many chain reactions. The mechanism by which this reaction proceeds is thought to involve four major steps



Reaction (16.11) is the initiation step, two free radicals are generated. Naturally, this is the slow step, requiring the breakage of a methyl bond from the diethyl ether. For a chain / radical reaction, initiation step is important as it is the starting point. Radicals are generated in the initiation step to allow the reaction to occur. In many applications, the initial radicals can be generated elaborately by using an initiator or substance that requires low energy to break into radicals. UV irradiation, reactor wall-surface construction and high-temperature (or heat) are common methods of promoting the initiation step.

Table 16.7 shows some of the bond energies that can be exploited for free-radical initiation. The carbon-iodate bonds are generally weak. The tertiary C-H bond in isobutane is fairly weak (404 kJ/mol) compared to other bonds in the molecule. Allyl and the benzyl bonds are of the lowest energy compared with others due to their π -electron sharing capabilities.

Steps (16.12) and (16.13) are propagation steps, with reactions occurring but a different free radical is produced while consuming one. The free radicals are not reduced by these reactions. The propagation steps are generally fast. Therefore, it is known that chain reactions are unlikely to stop until the reactants are exhausted.

TABLE 16.7 Bond energies.

<i>E</i> , kJ/mol	•H	•Cl	•Br	•I	•OH	•OCH ₃	•NH ₂	•CN	•NO ₂	•CH ₃	•CH ₂ CH ₃
methyl, CH ₃ •	438.9	350.2	302	241	385.3	348	356	512	255	377.0	372
ethyl, CH ₃ CH ₂ •	423	355	303	238	393	356	355	509	258	372	368
<i>i</i> -propyl, (CH ₃) ₂ CH•	413	356	309	238	400	359	360	506	263	371	364
<i>t</i> -butyl, C(CH ₃) ₃ •	404	355	304	233	401	351	359	493	263	366	358
vinyl, CH ₂ = CH•	463	382	338					556		424	418
allyl, CH ₂ = CHCH ₂ •	372		247	191	335			455		320	316
phenyl, C ₆ H ₅ •	472	406	351	280	470	423	436	561	303	433	428
benzyl, C ₆ H ₅ CH ₂ •	375	310	264	213	346		300		211	325	321
methoxy, CH ₃ O•	438					159			176	348	356
formyl, HC(O)•	368.6				458.1	417				354.8	348
acetyl, CH ₃ C(O)•	374	354	300	225	460	418	415			354	349

Source: Based on Blanksby S.J., and Ellison G.B., Acc. Chem. Res. 36 255-263, 2003.

The last step, (16.14) is the termination step, when two free radicals are combined to form a stable molecule. In this case, the termination step is the reverse step of the initiation step.

While the free radicals in the chain reactions are unstable and very active, there are substances that can adsorb free radicals and stop it from propagation. These substances are known as scavengers. Scavengers can be employed to stabilize chemicals that tend to decompose through chain reactions.

Chain reactions can also be very sensitive to the materials used for constructing the walls of the reactor because the adsorption and reaction properties of the walls in promoting or retarding termination and initiation steps depend on the nature of these surfaces. These effects have caused much difficulty in establishing the “true” rates of chain reactions and, more important, have led to accidents when chain reactions propagated unexpectedly because of unpredicted kinetics, which can be quite different from those obtained in a small lab reactor. One common difference is that lab data are frequently obtained in glass-walled vessels, which are quite unreactive, while large-scale reactors are frequently made of steel, whose walls have different reactivities.

Bioprocess engineers need to be strongly aware of the size effects in scaling-up any process that might involve chain reaction processes, for example, pyrolysis, gasification, and the more simple ones discussed earlier. The lab data, even if carefully obtained, may not explain large-reactor behavior. For a given reactor geometry, the wall surface area per volume is higher for smaller reactors. The rate of a chain reaction may be much higher in a large reactor. This might be good news unless the rate is too high and results in reactor runaway, where the temperature cannot be controlled. Similarly, one may be planning to run a process that does not occur by chain reactions, but in a large reactor a “side reaction” that occurs by a chain reaction could take over and dominate the process. Combining complicated kinetics with the possibility of thermal runaway can make engineers old before their time.

16.6 Autooxidation and safety

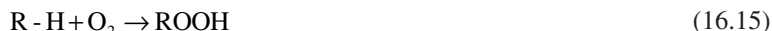
Everyone who works in a bioprocess or chemical laboratory is warned that organic chemicals should never be stored for long times because they can explode without warning or apparent provocation. Bottles of organic chemicals should always be disposed of within a few years, and, if a chemical is found that might be very old, a “bomb squad” of safety experts should be called to remove it and properly dispose of it.

Why do all organic chemicals just sitting around the laboratory at room temperature have the potential to explode spontaneously? The answer is that they can react with oxygen, in the air at room temperature in chain reactions to form organic peroxides, which can spontaneously react explosively upon shaking or opening the cap. Organic peroxides are examples of compounds that have fuel (C and H atoms) in the same compound with the oxidant, and these are solid and liquid explosives similar to dynamite and TNT.

In this section we will consider the mechanism by which a “harmless organic molecule” can react with oxygen at room temperature to form a potentially lethal system. Then we will discuss positive applications of this process, which are the primary processes by which such common chemicals such as acetone, phenol, isobutylene, styrene, and propylene glycol are made commercially.

16.6.1 A simple model of autooxidation

Consider any organic molecule, which we will call R-H, where R• could be an alkyl or any fragment containing C, H, and O atoms. In the presence of O₂ this molecule can undergo the autooxidation reaction



This reaction never happens significantly as a single step at any temperature because the R-H bond strength is > 330 kJ/mol for any C-H bond as shown in Table 16.7. However, consider the chain reaction sequence



If we add the second and third steps, we obtain the chain reaction



by which a hydrocarbon is converted into a peroxide.

The first step is a very slow dissociation step, with an activation energy > 330 kJ/mol. However, once the radical R• is made, it will rapidly react with O₂ to form the alkylperoxy radical, which is also very reactive and can abstract an H atom from any organic molecule in the solution to form the relatively stable (until someone shakes the bottle) alkyl peroxide.

We call this type of reaction autooxidation because it is an autocatalytic process (the reaction generates radical intermediates that propagate chain reactions) and it is an oxidation that converts alkanes into alkyl peroxides.

This chain reaction is just like those discussed previously, except now the reactants are an organic molecule and O₂, and the product is a potentially explosive hydroperoxide. It can be sketched as a chain in Fig. 16.6. The features of this chain reaction that make it so explosive are

1. Organic peroxides have high-exothermic heats of decomposition because they carry both fuel and oxidant in one molecule. We will discuss this part of the process (the explosion) later in this chapter.
2. The reactions can only occur if O₂ is present. A bottle of an organic chemical is perfectly safe for centuries if the cap is impermeable to oxygen, and is kept tightly fastened. (A cork is not a suitable cap.) However, one never knows whether someone may have left the cap off or loose for some time to allow the peroxide to form significantly.
3. This reaction depends crucially on the initiation step, and different molecules have vastly different capabilities of dissociation. The major problem here is that the initiation step can be initiated by a trace amount of an impurity that no one knows is in the bottle. As examples, all tertiary C-H bonds are fairly weak, as are the C-H bonds in aldehydes and alkenes. The reaction can be initiated by traces of these compounds, and the chain propagated throughout all molecules in the otherwise quite unreactive liquid.
4. The initiation step can be photoinduced. If a bottle is sitting in sunlight, UV photons (fluorescent lights are also more dangerous than incandescent lights) can cause photodissociation to initiate the chain reaction much faster than in the dark (this is the reason why many chemicals are sold in brown bottles).

Since one cannot be sure about the history of any old bottle of a chemical in a “common” laboratory, one should always dispose of old chemicals very carefully.

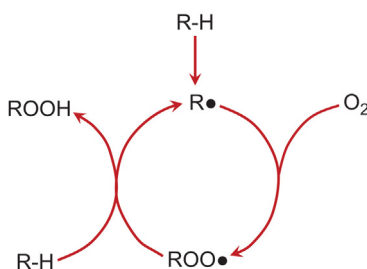


FIGURE 16.6 Chain reaction for alkane oxidation by autooxidation in which the alkyl and alkyl peroxy radicals propagate the chain, which is fed by the alkane RH.

16.6.2 Spoilage of food

Although not as dramatic as explosion, spoilage of food is a very important bioprocess issue in the food industry. This has two main forms—biological organism (bacterial, fungi or yeast) growth and oxidation.

In biological organism growth, improper sterilization during processing leaves organisms that reproduce and cause problems by creating large concentrations of organisms that taste bad or, even worse, make the consumer sick. In fact, as we will learn in Chapter 19 that no sterilization is absolute or 100%. Living organisms grow exponentially, so the concentration of microorganism biomass in foods are inherently unpredictable.

These organisms have two varieties, aerobic and anaerobic, signifying one grows with or another grows without oxygen. Aerobic microorganism growth is basically an oxidation process, but now the organism can be regarded as a catalyst for oxidation. Anaerobic organisms are in fact more dangerous than aerobic organisms because they tend to produce more dangerous toxins, such as botulism and salmonella.

Another significant spoilage mechanism of food is autooxidation. Here O_2 from air at room temperature causes oxidation of ingredients in food to produce molecules such as aldehydes and organic acids, both of which generally taste bad, although they are not usually toxic. The mechanism of food turning rancid is the same as we have discussed in this section: peroxide formation, which is autocatalytic, leading to rapid propagation. As in all these processes, the rate is controlled by traces of particular compounds that initiate peroxide formation, which then propagates throughout the food sample.

No amount of “sterilization” will prevent or even slow autooxidation, and there are only two defenses: removal of O_2 and addition of inhibitors. Oxygen barriers in food packaging are a major topic in the engineering of polymer films. The barrier properties of various polymers are very important in food applications, and many of these are multilayer polymers that have a thin layer of an impermeable polymer (such as polyacrylonitrile and ionic polymers) on a cheaper but O_2 -permeable polymer such as a polyolefin, which gives mechanical strength to the film.

The other method of oxidation prevention in foods is the addition of antioxidants. Nitrite solutions on meat or lettuce preserve the red or green color and make the package look fresher. The long lists of “additional ingredients” on packages of foods are either antioxidants or chemicals that inhibit bacterial growth. The phrase “all natural ingredients” on a package means that you need to be especially careful regarding spoilage.

One example of autooxidation you have experienced is the room-temperature oxidation of alcohol in wine. Within days and sometimes within minutes of opening a bottle of wine, the taste begins to deteriorate because of autooxidation. This converts the ethanol into acetaldehyde and to acetic acid. Wine lovers talk about letting the wine “breathe” after opening; so apparently some oxidation actually improves the taste. Distilled vinegar is made by the intentional oxidation of the alcohol in fermented apple juice into acetic acid, which can then be distilled from the juice and pulp.

Both biological reactions and autooxidation reactions in food are complex problems because both are highly autocatalytic. Their occurrence is therefore very variable between nominally identical samples of food. When a reaction is both unpredictable and intolerable, the bioprocess engineer must be especially alert.

16.6.3 Antioxidants

There is considerable hype in the popular culture about the role of antioxidants in promoting human health, from preventing cancer to slowing aging. These molecules presumably act to prevent autooxidation within our bodies. The processes are very complex and not well understood because they are different in different regions of our bodies and because the foods and additives we consume may be rapidly transformed into other molecules that may or may not be antioxidants. These molecules act as free-radical scavengers within our bodies, which prevent the chain reactions of autooxidation. Because these processes are so complex, no one knows how a particular chemical will act when ingested, and therefore additives can be sold that have no beneficial effect.

Room-temperature oxidation processes supply the energy by which we exist, but it is important that only the proper oxidation reactions occur in our bodies and not the ones that cause our skin to wrinkle and our brains to perform badly on exams. If you could come up with a chemical to assist in either of these, you could become very wealthy if you can avoid getting in trouble with the FDA.

16.7 Combustion

We will next consider the complexities of combustion, which are caused by the fact that combustion reactions are chain reactions. Combustion reactions are extremely fast and exothermic, and therefore, once the reaction is ignited, the process proceeds very quickly and becomes very nonisothermal. We will consider two exothermic chain reactions involving gases, the oxidation of H_2 and alkanes. Then we will consider combustion of liquid and solid fuels, a gas-liquid process. These processes all occur very rapidly and at very high temperatures.

TABLE 16.8 Reaction rates of the elementary steps in the $\text{H}_2 + \text{O}_2$ reaction

Reaction	$k_0, \text{L} \cdot \text{mole}^{-1} \text{s}^{-1}$	β	$E, \text{kJ mol}^{-1}$
1 $\text{O}_2 + \text{H} \cdot \rightarrow \cdot\text{OH} + \cdot\text{O}$	5.10×10^{13}	-0.82	69.1
2 $\text{H}_2 + \text{O} \cdot \rightarrow \cdot\text{OH} + \text{H}$	1.80×10^7	1.00	37.0
3 $\text{H}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$	1.20×10^6	1.30	15.2
4 $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{O}$	6.00×10^5	1.30	0.0
5 $\text{H}_2 + \text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{OH}$	1.70×10^{10}	0.00	200.0
6 $\text{H} \cdot + \cdot\text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	7.50×10^{20}	-2.60	0.0
7 $\text{O}_2 + \text{M} \rightarrow \cdot\text{O} + \cdot\text{O} + \text{M}$	1.90×10^8	0.50	400.1
8 $\text{H}_2 + \text{M} \rightarrow \cdot\text{H} + \cdot\text{H} + \text{M}$	2.20×10^9	0.50	387.7
9 $\text{H} \cdot + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 \cdot + \text{M}$	2.10×10^{15}	-1.00	0.0
10 $\text{H} \cdot + \text{O}_2 + \text{O}_2 \rightarrow \text{HO}_2 \cdot + \text{O}_2$	6.70×10^{16}	-1.42	0.0
11 $\text{H} \cdot + \text{O}_2 + \text{N}_2 \rightarrow \text{HO}_2 \cdot + \text{N}_2$	6.70×10^{16}	-1.42	0.0
12 $\text{HO}_2 \cdot + \text{H} \cdot \rightarrow \text{H}_2 + \text{O}_2$	2.50×10^{10}	0.00	2.9
13 $\text{HO}_2 \cdot + \text{H} \cdot \rightarrow \text{HO} \cdot + \cdot\text{OH}$	2.50×10^{11}	0.00	7.9
14 $\text{HO}_2 \cdot + \cdot\text{O} \rightarrow \cdot\text{OH} + \text{O}_2$	4.80×10^{10}	0.00	4.2
15 $\text{HO}_2 \cdot + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	5.00×10^{10}	0.00	4.2
16 $\text{HO}_2 \cdot + \text{HO}_2 \cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.00×10^9	0.00	0.0
17 $\text{H}_2\text{O}_2 + \text{M} \rightarrow \cdot\text{OH} + \cdot\text{OH} + \text{M}$	1.20×10^{14}	0.00	190.5
18 $\text{H}_2\text{O}_2 + \text{H} \cdot \rightarrow \text{H}_2 + \text{HO}_2 \cdot$	1.70×10^9	0.00	15.7
19 $\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2 \cdot$	1.00×10^{10}	0.00	7.5

16.7.1 Hydrogen oxidation

A “simple” prototype of combustion reactions is hydrogen oxidation,



However, this reaction is in fact extremely complex, and the standard model describing it consists of 38 reaction steps among 8 species— H_2 , O_2 , H_2O , H , O , OH , HO_2 , and H_2O_2 . Some of these reactions are listed in Table 16.8. Listed in Table 16.8 are the rate coefficients of the forward reactions shown. Rate constants are given in the form

$$k = k_0 T^\beta \exp(-E/RT) \quad (16.21)$$

All reactions are bimolecular. The 19 reverse reaction rate coefficients k_r are found from the equilibrium constants $k_r = k / K_{\text{eq}}$.

A simplified reaction scheme captures many features of this reaction. First, the reaction is initiated by generation of free radicals, with the lowest activation energy process being H_2 dissociation,



which is reaction 8 in Table 16.8. Next H atoms (or $\text{H} \cdot$) attack O_2 to produce $\text{O} \cdot$ and $\cdot\text{OH}$, both of which attack the parent molecules in the propagation steps



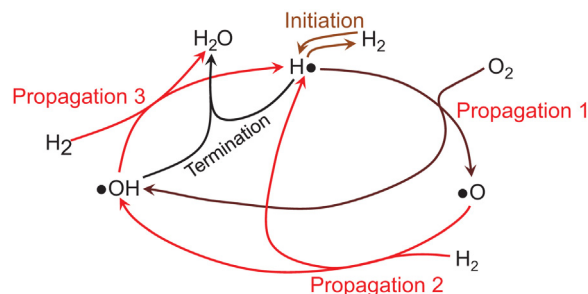
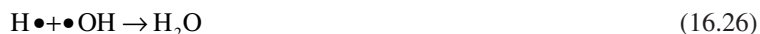


FIGURE 16.7 Sketch of chain reaction in $\text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}$. This is a highly simplified set of the reactions shown in the table. Which indicate the dominant chain reaction steps in forming water from three chain-propagating radical species: $\text{H}\cdot$, $\cdot\text{O}$, and $\cdot\text{OH}$.



These three reactions are propagation reactions, involving a free radical attacking a parent to form another free radical. Note that only the last reaction produces the stable product H_2O .

If we add another reaction



and add all four of the propagation reactions, we see that all the radical species cancel, leaving only the “simple” reaction



which is the stoichiometric reaction producing water from hydrogen and oxygen at high temperatures, although hydrogen peroxide H_2O_2 is also produced in measurable amounts in low-temperature processes. The reactions in this chain reaction are shown in Fig. 16.7.

This reaction sequence is similar to that described for diethyl ether decomposition to ethane and acetaldehyde: Reactions that produce stable products actually occur only through radicals attacking the parent and eventually producing the stable products (C_2H_6 , CH_3CHO , and H_2O in these examples).

However, the complete reaction mechanism of the hydrogen oxidation reaction is much more complex, both in its number of reaction steps, number of intermediates (OOH and H_2O_2), and observed behavior. A mixture of H_2 and O_2 can sit in a dry bulb for many years with absolutely no H_2O detected. However, if water is initially present, the reaction will begin, and if a spark is ignited or a grain of platinum is added to the mixture at room temperature, the reaction will occur instantly and explosively.

The reaction cannot begin without initiation of free radicals, and H_2 dissociation is very slow. Therefore, the few H atoms produced by the initiation steps may diffuse to the walls of the vessel and recombine before they can begin chain reactions. However, the presence of H_2O accelerates the rate of the reaction because it causes formation of traces of H_2O_2 , which easily dissociates and forms more $\text{H}\cdot$ and $\cdot\text{OH}$, which initiate the reaction by attack of H_2 and O_2 , and these reactions rapidly produce more radicals, which strongly accelerate the process.

A spark generates many radical species in the spark gap, and these can propagate radicals throughout the vessel. A platinum surface catalyzes the reaction (H_2 and O_2 readily dissociate on a Pt catalyst surface to begin the reaction), and the surface reaction then heats the Pt to a high temperature, where homogeneous reaction begins rapidly. Thus we see that premixed H_2 and O_2 mixtures behave very unpredictably. They are usually quite unreactive, but moisture or a trace chemical such as H_2O_2 , a spark, a trace of a catalyst (perhaps undetectable), or a hot surface can cause rapid and uncontrolled reaction.

The explosion limits of the $\text{H}_2 + \text{O}_2$ reaction have been studied thoroughly, and these limits exhibit an interesting variation with pressure. At low pressures the reaction is stable because radicals diffuse to the walls of the chamber and prevent chain branching, which leads to an explosion. At very high pressure radical quenching by diffusion to the walls is slowed down, and the heat released by the reaction leads to a thermal explosion (Fig. 16.8).

The boundaries between stable flames and explosions are very “fuzzy” because they depend on traces of chemicals in the vessel, which may act as initiators or scavengers, and they depend strongly on the size and composition of the walls of the vessel. These diagrams are shown to illustrate the complexities in predicting the behavior of any chain reaction, even a “simple” one such as $\text{H}_2 + \text{O}_2$.

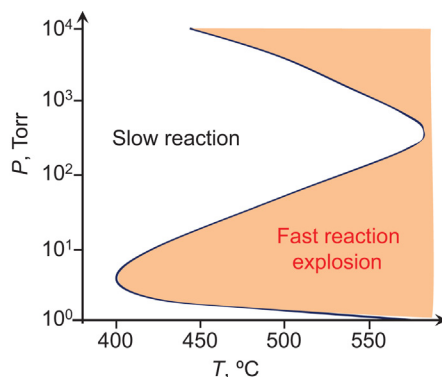


FIGURE 16.8 Explosion limits of the $\text{H}_2 + \text{O}_2$ reaction. At low pressures explosion is determined by the quenching of chain branching of radicals at the walls of the vessel, while at high pressures the larger rate of heat generation leads to a thermal explosion.

16.7.2 Chain branching reactions

In the reaction steps for H_2 oxidation the first two reactions are chain branching reactions, with one radical species producing two other radicals every time a reaction event occurs. The first of these probably proceeds by the steps



and the hydroperoxy radical $\bullet\text{OOH}$ reacts immediately at high temperatures but can be observed in finite concentrations at low temperatures.

Note that this reaction produces two reactive free radicals from one. We call these chain branching reactions because the propagation steps produce more radical species than they start with. Thus the propagation steps can also increase the concentration of free radical species, and further destabilize the kinetics. We call a propagation step in which one radical species is produced for each radical reacting a linear chain, while a process that produces more radicals is called a branched chain. These are sketched in Fig. 16.9.

Most combustion reactions involve chain branching reaction steps. Under conditions where these steps are less significant than linear chain reactions, the reaction appears to be stable, but when the chain branching steps dominate, the overall reaction rate can accelerate uncontrollably.

Recall that in autooxidation discussion, hydroperoxide species were sufficiently stable at low temperatures that only linear chains formed. When the bottle of peroxides explodes, chain branching steps such as



begin to become significant. This is a chain branching reaction because one radical-prone molecule produces three radicals. The rapid rise in the concentration of radical species can accelerate the decomposition reaction of a bottle containing peroxide rapidly and catastrophically.

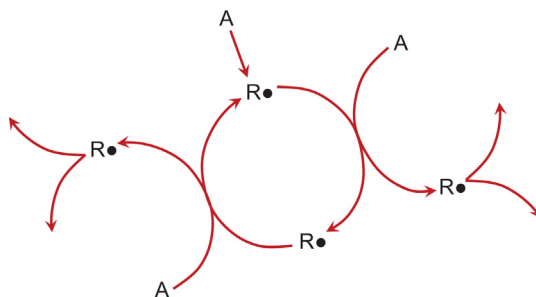


FIGURE 16.9 A schematic of chain branching reactions where the propagation steps produce more than one radical so that the process tends to grow exponentially, leading to a rapid acceleration of the reaction and possibly a chain-branching explosion.

16.7.3 Alkane oxidation

One of the most important combustion reactions in industry and in home heating is natural gas combustion,



The transportability of natural gas in pipelines and the clean combustion in its oxidation make it the fuel of choice in many applications.

As one might guess from our previous example of H_2 oxidation, this reaction is extremely complex. The standard model involves over 300 reaction steps among approximately 30 chemical species. Here even the stable product species can be complex, with CO , HCHO (formaldehyde), and soot (carbon) being among the highly undesired pollutants in CH_4 combustion. Since H_2 , O_2 , and H_2O are involved as intermediates and products, the 38 reaction steps in the $\text{H}_2 + \text{O}_2$ reaction listed previously are in the set of the reactions that involved in CH_4 oxidation.

We will not attempt to describe the mechanism of this process except to note that an important initiation step is CH_4 dissociation,



with the $\text{H}\bullet$ and the $\bullet\text{CH}_3$ active to attack O_2 and begin propagation steps.

Mixtures of natural gas and air are similarly unpredictable, being quite stable and unreactive until a spark or a hot surface ignites reaction, and then thermal and chain branching autocatalysis takes off and so does the building.

Similar mechanisms (but even more complex) operate in the combustion of higher hydrocarbons. Initiation is easier because the C-H bonds can be weaker. The $\text{CH}_4 + \text{O}_2$ reactions are a subset of all hydrocarbons since CH_4 is one of the possible decomposition products of higher hydrocarbons.

One much employed example is combustion of gasoline in the engine cylinders of an automobile. Here the fuel is injected into the combustion chamber as a vapor with air at nearly the stoichiometric composition for complete combustion, and a spark ignites the mixture to create pressure, which forces the piston down. Details of ignition reactions determine issues such as engine knock or flooding, with branched aliphatic and small fuel molecules being advantageous for both of these problems. High-octane alkanes produce fewer chain branching radicals during the compression of the air—fuel mixture, and this avoids engine knock, which will occur if ignition occurs spontaneously before the spark plug fires to ignite the alkane—air mixture at the start of the power stroke.

16.7.4 Liquid alkane oxidation

In the diesel engine, the jet engine, and kerosene combustion, liquid fuel is sprayed into the combustion chamber with air, and the liquid is not totally vaporized before ignition. Therefore, in drop combustion there are flames around the liquid drops that shrink as the reaction proceeds.

We note finally that for most of these processes no one knows their kinetics. Rates have been measured with great precision in the laboratory under specific conditions, but in engineering applications the processes are so complex that these kinetics are not useful. In almost all situations the rates of reaction are controlled by mass and heat transfer rates, and the fluid flow is turbulent. As the actual reaction steps depend on mass transfer (ignition by initiators and termination reactions at surfaces), it is a very complicated problem.

The complexity and importance of combustion reactions have resulted in active research in computational chemistry. It is now possible to determine reaction rate coefficients from quantum mechanics and statistical mechanics using the ideas of reaction mechanisms as discussed in Chapter 6. These rate coefficient data are then used in large computer programs that calculate reactor performance in complex chain reaction systems. These computations can sometimes be done more economically than to carry out the relevant experiments. This is especially important for reactions that may be dangerous to carry out experimentally, because no one is hurt if a computer program blows up. On the other hand, errors in calculations can lead to inaccurate predictions, which can also be dangerous.

16.7.5 Thermal ignition

Most chemical accidents have occurred because some of these effects were not expected or accounted for, and most of the research on combustion processes originated in an effort to explain the unexpected and potentially hazardous. Thermal ignition contributes another safety hazard in combustion processes.



FIGURE 16.10 Open burning of biomass. Fuel biomass on the surface of the “pile” burns as oxygen is available. More burning results in higher temperature and thus catalyzes more burning if oxygen supply is abundant. (A) Burning of hay. (B) Burning of wood pile. (C) Forest fire.

Our first example of a chain reaction, the decomposition of diethyl ether to ethane and acetaldehyde, is endothermic; so the reactor tends to cool as reaction proceeds. However, the oxidation of H_2 is exothermic by 238 kJ/mol of H_2 , and the oxidation of CH_4 to CO_2 and H_2O is exothermic by 803 kJ/mol of CH_4 . Thus, as these reactions proceed, heat is released and the temperature tends to increase (strongly!). Thus, thermal ignition is very important in most combustion processes.

In addition to ignition of gases, liquids and solids can also exhibit ignition phenomena. A classic example is the “spontaneous combustion” of oily rags containing paint solvents or automobile oil. One does not want to store large quantities of these rags together, because they can suddenly heat up and catch fire. Another example is the “spontaneous combustion” of coal piles and of underground coal fields. A large pile of coal will almost inevitably catch fire and burn, and barges of coal must be transported and unloaded quickly or the barge will begin to burn, a quite unpleasant experience for the sailors, especially if far from port.

For a pile of wood, coal, or hay, the burning stability is dependent on the temperature, moisture, and spark. Assuming that the pile is reasonably large, the limitation would be oxygen availability. Fig. 16.10 shows some of the examples of uncontrolled or open biomass burning. In this case, one could use a simple CSTR model to describe the burning of a pile of biomass or coal. The feed (reactant) to the reactor is air or O_2 , and the products are CO_2 , CO , and H_2O .

We have already dealt with nonisothermal reactors and their effects in Chapters 16 and a brief review in Section 16.3. The major and potentially most dangerous application of these effects is in combustion reactors. Consider our standard CSTR with parameters as indicated in Fig. 16.11.

Recall from Chapter 15 that the steady-state energy-balance equations in a CSTR can be reduced to a single equation, which we wrote by considering the rates of heat generation and removal. We write this, from Eq. (16.1), as

$$Q \sum_{j=1}^{N_s} C_{j0} C_{pj} (T - T_0) + U A_H (T - T_a) = A_B (-\Delta H_R) r''(C_A, T) \quad (16.31)$$

where U is the effective heat transfer coefficient, A_H is the heat transfer area, A_B is the surface area of the biomass (or coal) pile, r'' is the rate of reaction based on surface area, and reactant (or species) A refers to oxygen (O_2). We then rearranged this equation to become Eq. (16.5) or

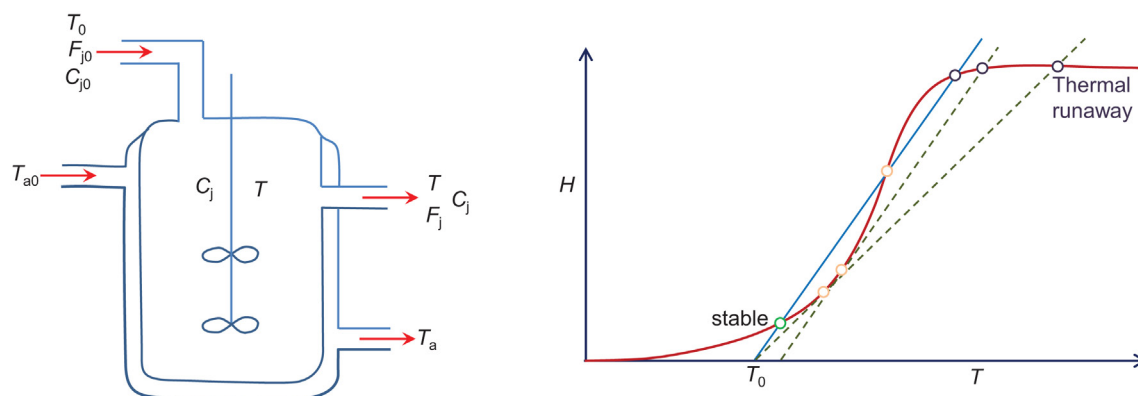


FIGURE 16.11 Heat generation and removal for combustion reaction in a CSTR. When the feed temperature increases (or feed rate decreases) slightly, the rate can go from nearly zero to nearly completion when the heat removal (*straight*) line becomes tangent to the heat generation curve, and the steady-state temperature jumps to a high value.

$$H_R(T) = H_G(T) \quad (16.32)$$

and we constructed a graphical solution by plotting the left-hand side $H_R(T)$ and the right-hand side $H_G(T)$ versus T , as repeated in Fig. 16.11.

Consider an oxidation reaction in this CSTR. Suppose we begin at the lower steady state, where the reaction rate and the rate of heat generation are very low. If the feed temperature T_0 and the wall temperature T_a are low, there is little reaction, and we would detect negligible temperature change. However, if we increase T_0 or T_a , slightly (and the straight line moves right ward in parallel as shown in dashed line), the system can jump to the upper steady state. Alternatively, if the feed rate is decreased and the straight line has decreased slope (also shown as dashed line passing through T_0), the system jumps to the upper steady state. These situations have been discussed in Chapter 15.

If this is a combustion process in which the rate has a very large effective activation energy, H_R is very large and negative, and $Q\Sigma C_{j0}C_{Pj}$ is small (undiluted gases), then these effects become very large. One therefore observes a situation where the rate is effectively zero for one temperature because the effective activation energy is very large, but a slight change in any parameter can cause the system to jump to the upper steady state, where the reaction goes to completion and the temperature goes to the adiabatic flame temperature.

For H_2 or CH_4 in air near stoichiometric compositions (28% H_2 , in air and 9.5% CH_4 in air, respectively), the temperature jumps from ambient to $>2000^\circ$ (it does not make much difference whether one uses $^\circ C$ or K units for this calculation), and the reactor almost certainly explodes.

For a coal pile, dry wood pile or a barrel of oily rags, there is a slow flow of air through the pile or reactor with a large residence time, and processes are slow enough (an autooxidation process) that the composition is nearly uniform. A slight increase in temperature (perhaps a warm day) can cause the rate of oxidation of the alkane in the oil or the carbon in the coal or the biomass in wood to oxidize, and at some T_0 , the “reactor” will suddenly ignite and burn. Once this happens, natural convection forces air rapidly through the barrel or coal pile and “fans” the flame. Underground coal fields are especially difficult to extinguish because there are many holes in the ground which act as inlets and outlets for the “reactor”.

While the CSTR model is extremely primitive, the ideas of size dependence and differences in rate for air flow before and after ignition explain many of the features of these troublesome chemical reactors.

16.7.6 Thermal and chemical autocatalysis

So far we have seen examples of thermal and chemical autocatalysis in Chapters 8 and 16. The thermal autocatalysis can be viewed through the Arrhenius law,

$$k = k_0 \exp(-E/RT) \quad (16.33)$$

where reaction rate (constant) increases exponentially with increasing temperature. When heat is generated (exothermic reactions), temperature rises in the reactor and thus increases the reaction rate. In return, faster heat generation is expected. This is the thermal autocatalysis.

In hot-water extraction example described in Chapter 8, the catalyst proton H^+ (or H_3O^+) was generated during the extraction reactions. In Chapters 13 and 14, we examined the cell growth. Cell is produced and it is also the catalyst for more growth. These reactions can be modeled as



because the reaction generates the catalyst after we added the catalyst to initiate the process. Another example was the chain branching reaction such as



just described in hydrogen oxidation. The bioreactions were nearly isothermal, but combustion processes are both chain branching and autothermal, and therefore they combine chemical and thermal autocatalysis, a tricky combination to maintain under control and of which bioprocess engineers should always be wary.

This suggests immediately the definition of autocatalysis. A reactive intermediate or heat can act as catalysts to promote the reaction or more precisely increase reaction rate. However, in contrast to conventional catalysis, we do not add the catalyst from outside the system, but the catalyst is generated by the reaction. We may add promoters or heat to initiate the process, which then accelerates by autocatalysis. Conversely, we may add inhibitors or cool the reactor to prevent both types of autocatalysis.

The best inhibitor of autocatalysis is to have a small system. Surfaces act as both sinks of free radicals to increase termination and as sinks of heat (larger heat transfer area) to prevent thermal runaway, and small systems have large surface-to-volume ratios to prevent these runaway possibilities.

16.8 Premixed flames

In this section we consider the combustion of premixed gaseous fuel and air mixtures. Consider first the laboratory Bunsen burner one can see frequently in a biosafety cabin / workstation, shown in Fig. 16.12. Natural gas from the gas supply system enters the bottom of the burner, where it is mixed with air, with flow rates adjusted by the gas valve and holes in the bottom of the burner, where air is sucked in by natural convection. The premixed gases travel up the barrel of the burner (a tubular reactor), and, if flows are suitably adjusted and a match has been used to ignite the mixture, a stable flame forms at the top of the tube.

If the flow rate is too low, the flame will flash back and propagate back up the tube to the mixing point and extinguish. If the flow rate is too high, the flame will lift off the top of the tube and either extinguish or burn as a turbulent lifted flame.

16.8.1 Stability of a tube flame

You have probably noticed that it is nearly impossible to maintain a stable flame within the tube of a Bunsen burner; it will either burn at the top or flash back to the mixing point. There is usually no stable steady state for a flame reaction in a straight tube.

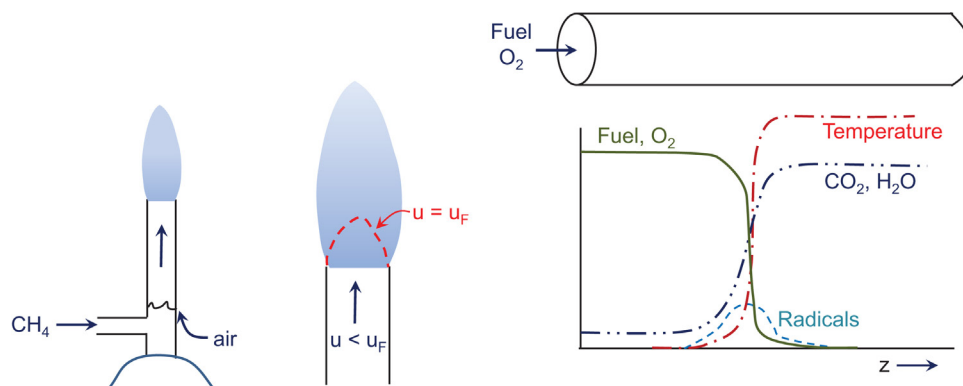


FIGURE 16.12 Bunsen burner, which is a typical premixed flame in which the flame velocity u_F equals the flow velocity u in the expansion at the end of the tube, creating a stable flame.

This points out several major characteristics of premixed flames—(1) They cannot be controlled stably within a constant-diameter tubular reactor configuration; and (2) the chain branching reactions and the heat release tend to make them either blow out or flash back into the tube and extinguish.

Flames are characterized by a flame velocity u_F , which is the velocity with which a flame front will move down a tube containing stagnant premixed gases. The upper and lower compositions where the flame velocity goes to zero are called the flammability limits, and the flame velocity is usually its maximum near the stoichiometric composition for CO_2 and H_2O formation.

The reason why it is difficult to sustain a flame within a tube is that the flame will only be stable if

$$u = u_F \quad (16.35)$$

where u is the flow velocity for the PFR. It is virtually impossible to adjust the flow velocity to be exactly u_F . Even if this occurs, the flame is only neutrally stable; it will drift up or down the tube.

Flow in the tube will be parabolic if the flow is laminar ($\text{Re} < 2100$), and thus gases near the center of the tube may propagate downstream, while gases near the wall propagate upstream toward the mixing point. This further destabilizes a premixed flame within a tube.

16.8.2 Premixed burner flames

Premixed flames can only be stabilized by providing an expansion section in the tube where the cross section increases so that u slows, creating a zone where $u = u_F$ and a flame is stable. In a Bunsen burner this is achieved quite simply by having the flame height vary as u changes within the tube so that a burning surface (roughly a cone) is maintained stable over a large range of flow rates. At the exit of the tube the flow velocity decreases over a wide range so that the flame is quite stable.

The other stabilizer of flames is cold surfaces. These act to lower u_F in the region of the surface and thus create a stable edge to the flame at the wall of the burner. This occurs both by thermally quenching the reaction near the surface and by quenching free radicals by adsorption on the surfaces, which stops the combustion reactions.

One very important device that uses this principle is the flame arrestor, which is inserted in pipes to prevent flames from propagating between pieces of gas-handling equipment. These are usually metal shavings (steel wool) inserted in tubes at strategic distances to stop any flames that may travel down the tube.

16.8.3 Diffusion flames

When the air inlet is shut off in a Bunsen burner, the flame can still be maintained, but it switches from the blue color of a normal CH_4 flame to the yellow of a diffusion flame. This is the situation of a gas stove. Now pure CH_4 flows up the tube, and the O_2 from outside the tube is mixed with CH_4 just above the tube, with flow of air driven by natural convection below the hot product gas mixture.

This burner, a butane lighter, a candle, a burning log, and a match (after ignition) are all examples of diffusion flames where one generally provides the fuel and relies on natural convection of air to provide the oxidant.

Diffusion flames are much more stable than premixed flames because the rate of the reactions is limited by the supply of air and its diffusion into the fuel region to form the flame front. Several examples of diffusion flames are given in Fig. 16.13. These all typically have cylindrical symmetry, with air surrounding the fuel in the center. The cylindrical laminar flame is simplest to sketch because it is two dimensional in composition (direction of flow z and radial position from the center r), with composition profiles as shown in Fig. 16.14. Gaseous fuel and air are admitted through separate slots, and the reaction proceeds along the line of contact. The gases are convected in the vertical flow z -direction, and horizontal diffusion (x) between the fuel and air create the flammable mixture.

One can model this system in principle using the differential mass- and energy-balance equations written with the principles shown in Chapter 3 with flow in the z direction and diffusion in both the flow direction and the lateral x direction to obtain profiles of $C_A(z, x)$ and $T(z, x)$. One can see immediately that this will be a very complex mathematical problem to solve because there are many species (at least 30 for natural gas flames), but the problem will be made even more complex because of natural convection. Since the temperature in the flame varies from 25 to $>2000^\circ\text{C}$ in short distances, the density in and above the flame decreases dramatically (by nearly a factor of 10), and this causes large buoyancy effects, which accelerate the gases in the vertical direction. This provides the air flow in many diffusion flames, but it can also create turbulence, which causes greatly enhanced mixing or flow-induced diffusion / dispersion above that which would occur by molecular diffusion.

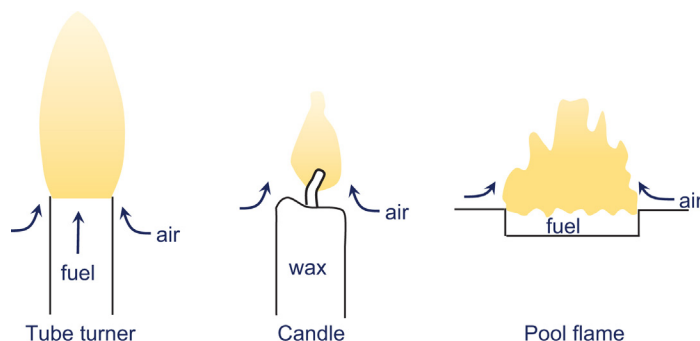


FIGURE 16.13 Some typical diffusion flames in which gas or liquid reacts with O_2 from air. The reaction occurring at the region where mixing occurs.

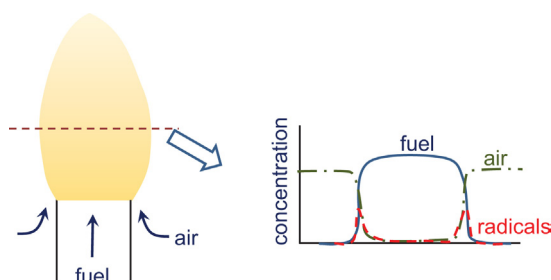


FIGURE 16.14 Concentration profiles in a diffusion flame such as a candle. Radical intermediates that propagate the flame have high concentrations in the flame zone between fuel and O_2 .

16.8.4 Laminar and turbulent flames

There is another distinction between flames: laminar versus turbulent. Small flames are generally steady and laminar, while large flames exhibit visible turbulent eddies. Candles and fireplaces are well-known examples where in still air the flame is steady, but, when there is wind or one blows on the flame, the flame flickers.

One can describe these phenomena through the Reynolds number (forced convection) and Rayleigh number (natural convection), but the reader can see immediately that the situations are so complicated that correlations in elementary texts on fluid flow are not easily applicable to predicting flame behavior. Reactive flows are among the most complex problems in modern engineering.

16.9 Heat generation

Heat considerations give the first estimate of the characteristics of combustion. As discussed in Chapters 3 and 4, the adiabatic reaction temperature (frequently called the adiabatic flame temperature) gives an approximation to the final temperature,

$$\Delta T = \frac{-\Delta H_R}{\sum_{j=1}^{N_S} n_j C_{Pj}} \quad (16.36)$$

We need to be especially careful in using this equation to try to describe combustion accurately. Since the final temperature is so large, the heat capacity C_p is not at all constant. Further, there are many reactions and products in flames, and one has to use the multiple-reaction version of this equation for accurate calculations. The intermediates, which are at negligible concentrations at low temperature, have significant concentrations at high temperatures. For example, the water dissociation reaction



has an equilibrium constant that predicts considerable $H\bullet$ and $\bullet OH$ in the high temperature of most flames.

16.9.1 Radiation

Another consideration in flames is radiation. The light that one sees in a flame is mostly fluorescence from the radiation of particular radical species formed in electronically excited states. (The blue color from CH_4 flames is CH^\bullet emission). Gases also radiate blackbody radiation, primarily in the infrared. The glow from burning wood or coal is blackbody emission radiated from the surface.

The emission observed from cracks in a burning wood surface is brighter because the emission from a cavity has the equilibrium blackbody distribution, which is independent of the emissivity of the surface. Also most of the heat from a campfire is from radiation if you are beside the fire. The air beside the campfire is close to the ambient temperature because natural convection is drawing it up into the rising flame.

Most of the emission from combustion processes is in the infrared and is not visible, but a large fraction of the energy carried off from combustion processes is in the form of radiation heat transfer.

16.9.2 Flammability limits

In practice there is only a certain range of compositions where premixed gases will burn. There is obviously a great deal of interest in this composition because it sets the limits of operation of many processes. The ignition limit is only loosely defined because it depends sensitively on temperature, flow conditions, and the presence of trace chemicals in the fuel, which can act as flame initiators or inhibitors by enhancing or slowing either rate of initiation or rate of termination.

A very important consideration in flammability is the presence of surfaces. Cold surfaces act as free-radical quenchers and maintain the gas temperature below the ignition temperature, while hot surfaces can act as ignitors.

Many of the industrial accidents in the chemical industry have originated from reaction systems that were quite stable in small containers but exploded when larger reactors were used.

16.10 Gasification and pyrolysis

One of the traditional ways of generating heat and power for human use is by burning a fuel. Solid wood and coal have been very important fuels since our cave-dwelling ancestors, and both are still important fuels in heating and power generation. Their combustion has characteristics that are common to most solids combustion processes.

The reduction of solid mass or liquid drops during pyrolysis/gasification/combustion can be modeled based on surface reactions. Two scenarios could emerge during pyrolysis: shrinking core (or systematic burning of biomass) or selective depletion (slow pyrolysis or carbonization).

Fig. 16.15 shows the “Shrinking-core” model of biomass peeling away during pyrolysis – gasification process. It is not difficult to imagine that the reaction rate is simply proportional to the exposed surface area if the molecules are assumed to be identical, i.e.

$$r_x = -kS = -4\pi kR^2 \quad (16.38)$$

where r_x is the biomass generation rate; k is the specific reaction rate constant; S is the surface area (exposed), and R is the remaining radius of the biomass particle (assuming spherical shape).

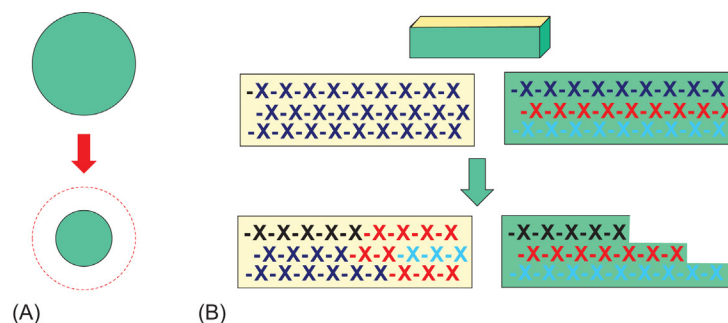


FIGURE 16.15 The “shrinking-core” idealization of biomass gasification / liquefaction. The molecules located on the extreme outer layer of the surface is shown as *dark-blue X*, the layer immediately down the first is shown as *red X*, while the layer next to the second layer is shown as *X*; ... The molecules can be “peeled” away one layer at a time as shown on (B), *right view*. Total exposed surface molecules are not changing if the surface is “flat” as illustrated on (B), *left view*; Peeling away of surface molecules. If all the molecules are equally “peelable” and not affected by the “peeling” of other molecules, the overall process may be modeled as a “Shrinking-core” shown on (A) for a *round* particle; Shrinking-core or decreasing particle size.

In most applications, we do not need the detailed particle size change. In this case, the particle size change can be related to the conversion easily

$$f_x = \frac{R_0^3 - R^3}{R_0^3} = 1 - \left(\frac{R}{R_0} \right)^3 \quad (16.39)$$

where R_0 is the initial particle size. That is

$$\frac{R}{R_0} = (1 - f_x)^{1/3} \quad (16.40)$$

Substituting Eq. (16.40) into Eq. (16.38), one obtains

$$r_x = -kS_0 (1 - f_x)^{2/3} \quad (16.41)$$

where S_0 is the initial surface area of the biomass particle.

As illustrated in Fig. 16.16, the pyrolysis residual biomass yield decreases with time, while the available vaporizable components also changes with time. As a result, the residual biomass increasingly becomes a porous matrix of carbonized materials. Similar to Eq. (16.38), one can envision that the reaction rate or loss of biomass rate is proportional to the exposed surface area. However, the exposed surface area is no longer a simple relation as shown in Eqn (16.38). At the start of the reaction, there is a portion of the particle surface that is equally peelable, which goes true for the out boundary of the “non-touched” core shrinks. However, there are surface molecules exposed within the remaining matrix that are left-over that are still peelable. Therefore,

$$r_x = -kS = -k \left[\epsilon_0 4\pi R^2 + a \left(1 - \epsilon_0 \right) \left(1 - \frac{R^3}{R_0^3} \right)^n \right] \quad (16.42)$$

where x is the radius of the “shrinking-core” of biomass that has not subjected to pyrolysis peeling; ϵ_0 is the initial portion of exposed molecules that are “equally” peelable; a is the (internal) surface area of the porous matrix after pyrolysis; and n is the power-law index of the fraction of peelable molecules on the internal surface.

The application of Eq. (16.42) is more difficult than Eq. (16.38) for the case where no “skeletal” matrix leftover on top of the shrinking-core. Because of the “skeletal” matrix, the conversion of biomass can be computed by

$$f_x = \frac{R_0^3 - R^3 - (1 - f_{\max} - \alpha)(R_0^3 - R^3)}{R_0^3} \quad (16.43)$$

where f_{\max} is the maximum conversion can be achieved and α is the fraction of “peelable” components left inside the “skeletal” remains. The value of α should lie between 0 and $(1 - f_{\max})(1 - \epsilon_0)$. A first order approximation leads to

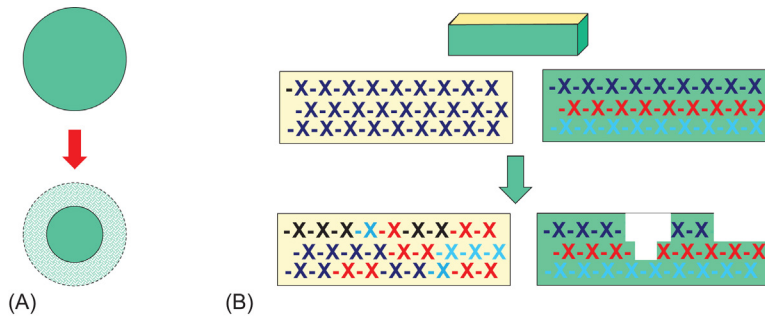


FIGURE 16.16 The “vaporization” of gasifiable components on the biomass surface leaving an increasingly “hardened” non-vaporizable “skeletal” matrix of carbonized materials over an intact core. (A) Shrinking-core or skeletalization. (B) Peeling away of surface molecules.

$$\alpha \approx (1 - f_{\max})(1 - \varepsilon_0) \left(1 - \frac{f_X}{f_{\max}} \right) \quad (16.44)$$

From Eqs. (16.43) and (16.44), one can obtain

$$\frac{R}{R_0} = \left(1 - \frac{f_X}{f_{\max} + \alpha} \right)^{1/3} \approx \left[1 - \frac{f_{\max} f_X}{f_{\max}^2 + (1 - f_{\max})(1 - \varepsilon_0)(f_{\max} - f_X)} \right]^{1/3} \quad (16.45)$$

which can be employed to approximate the rate expression to yield

$$r_X = -k \left\{ \varepsilon_0 S_0 \left[1 - \frac{f_{\max} f_X}{f_{\max}^2 + (1 - f_{\max})(1 - \varepsilon_0)(f_{\max} - f_X)} \right]^{\frac{2}{3}} + a(1 - \varepsilon_0) \frac{f_{\max} f_X}{f_{\max}^2 + (1 - f_{\max})(1 - \varepsilon_0)(f_{\max} - f_X)} \left[1 - \frac{f_{\max} f_X}{f_{\max}^2 + (1 - f_{\max})(1 - \varepsilon_0)(f_{\max} - f_X)} \right]^{n/3} \right\} \quad (16.46)$$

Therefore, the biomass depletion rate has an apparent order less than 1. When

$$\varepsilon_0 = 1 \text{ and } f_{\max} = 1,$$

Eqs. (16.42) and (16.46) reduce to (16.38).

During batch pyrolysis/gasification/combustion of biomass or fuel particles, mass balance leads to

$$M_0 \frac{df_X}{dt} = -r_X \quad (16.47)$$

For a given temperature profile, i.e. $T = f(t)$, one can integrate Eq. (16.47) to obtain the conversion as a function of time, thus the residual biomass as a function of time.

16.10.1 Pyrolysis

The first step when coal or wood particles (we call them chunks or powder and logs or chips, respectively) burn is pyrolysis, in which heat causes the water and volatile organics to evaporate. These gases then burn in oxygen in the boundary layer in the first stage of burning.

Coal and wood decompose to give many small organic molecules such as alkanes, aromatics, alcohols, aldehydes and ketones, and organic acids. As an example, methanol is still sometimes called wood alcohol because it was first obtained by heating wood in a kiln and condensing the products, one of which was methanol. In the nineteenth century, coal and wood were the major sources of many chemicals such as acetic acid and acetone, and coal was a major source of chemicals such as benzene. As noted previously, one of the types of products from coal was highly colored chemicals, and these were called coal tars, from which highly colored dyes could be extracted. The search for reliable and cheaper sources of these dyes produced the development of organic chemistry for the systematic search for new colored dyes, and this led to the giant European chemical companies such as AkzoNobel and BASF.

Pyrolysis of biomass has gained interest again in the twenty-first century with the public awareness of CO₂ and climate change. Biomass can be pyrolyzed to produce liquefied carbohydrates, which can be further converted to liquid fuel and chemicals. Slow pyrolysis carbonizes more while fast pyrolysis produces more vapor products as shown in Fig. 16.16.

Woody biomass has an approximate stoichiometry of CH_{1.4-1.6}O_{0.65-0.7}. It still requires oxygen to burn. In the biomass energy applications studied today, the energy value is desired to be kept in the final products and thus less oxygen addition is desired. Addition of oxygen is only used to provide heat for raise the system temperature. Thermal or hydrothermal treatment of woody biomass can be applied in a wide temperature ranges. Torrefaction occurs between 200°C and 320°C, when the solid material is partial carbonized by devolatilizing the biomass. Commercial pyrolysis is normally carried out

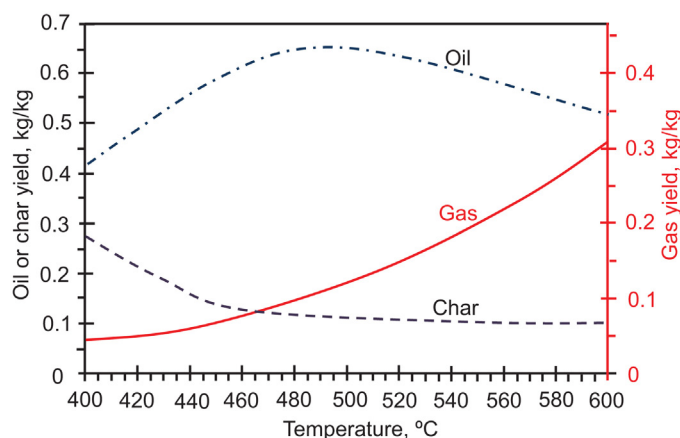


FIGURE 16.17 Pyrolysis of woody biomass. For char (solid fraction) productions, the pyrolysis is under low temperature (usually < 400°C) with long residence time, whereas fast pyrolysis (< 1 s) at about 500°C is ideal for liquid (“oil”) production.

under oxygen-lean environment, below a temperature of 600°C. As the temperature is increased, more gas products are produced. Gasification is normally conducted between 700°C and 1000°C.

Pyrolysis of woody biomass produces char (solid residue), liquid (bio-oil or oil), and gas (or syn-gas). Fig. 16.17 shows the typical yields of pyrolysis as a function of pyrolysis temperature. Table 16.9 shows typical compositions and yields of pyrolysis of switchgrass.

During pyrolysis, each component pyrolyzes differently. Cellulose undergoes cracking of glycosidic bonds to produce levoglucosan and isomers (up to 80% conversion in the absence of alkali metals) as well as ring-opening and reforming to produce low-molecular weight oxygenates (acids, aldehydes, ketones), furfural and HMF, heterocyclic compounds, etc. Hemicellulose thermal cracks to furans and to sugars in the absence of alkali metals. Lignin is rendered to pyrolytic lignin (relative large molecules). Pyrolysis reactions of biomass are catalyzed by alkali metal salts. One can expect less liquid production when alkali metal salts are present.

Table 16.10 shows the elemental composition of the whole pyrolysis oil (aqueous phase + oil phase) as well as those of the original switch grass. One can observe that the oil is slightly less oxygenated than the switchgrass itself. The two phases of the oil has very different densities: 1100 kg/m³ for aqueous phase and 920 kg/m³ for the oil phase.

TABLE 16.9 Pyrolysis products from Switchgrass.

Pyrolysis T, °C	Char yield, kg/kg	Biooil yield, kg/kg		Syngas						
		Oil phase	Aqueous phase	Yield, kg/kg	H ₂ , %	CO, %	CH ₄ , %	CO ₂ , %	C ₂ H ₄ , %	C ₂ H ₆ , %
400	0.48	0.04	0.18	0.08	28.0	21.7	39.2	9.1	1.2	0.8
500	0.42	0.07	0.20	0.09	25.4	21.5	39.4	9.4	2.3	1.9
600	0.25	0.12	0.25	0.26	9.7	27.7	16.6	33.2	4.3	7.0

Source: Data source: Imam T. and Capareda S. 2012 J. Anal. Appl. Pyrolysis. 93 170–177.

TABLE 16.10 The elemental composition of switchgrass and its pyrolysis oil (produced at 600°C).

Element	C, kg/kg	H, kg/kg	O, kg/kg	N, kg/kg	S, kg/kg
Switch grass	0.42	0.061	0.474	0.004	0.001
600°C-pyrolysis oil	0.50	0.093	0.37	0.015	0.006

Source: Data source: Imam T. and Capareda S. 2012 J. Anal. Appl. Pyrolysis. 93 170–177.

TABLE 16.11 Pyrolysis of switchgrass, approximate Roels's formulae $\text{CH}_{1.73}\text{O}_{0.77}\text{N}_{0.01}$, under oxygen lean conditions. Chemical characteristics of switchgrass biochar produced under various thermal conditions and residence times.

Characteristics	C %	H %	O %	N %	S %	Roels' formula	Air loading, kg-air/kg-biomass	
300°C	1 h	48.3	5.6	42.0	0.63	0.14	$\text{CH}_{1.4}\text{O}_{0.77}\text{N}_{0.01}$	5.89
	2 h	48.5	5.6	42.3	0.60	0.12	$\text{CH}_{1.39}\text{O}_{0.65}\text{N}_{0.01}$	5.87
	3 h	48.8	5.9	41.6	0.63	0.15	$\text{CH}_{1.45}\text{O}_{0.64}\text{N}_{0.01}$	6.04
350°C	1 h	48.4	5.7	42.4	0.72	0.15	$\text{CH}_{1.40}\text{O}_{0.66}\text{N}_{0.01}$	5.85
	2 h	53.2	5.4	37.9	0.84	0.14	$\text{CH}_{1.21}\text{O}_{0.53}\text{N}_{0.01}$	6.51
	3 h	52.7	5.3	39.0	0.91	0.12	$\text{CH}_{1.21}\text{O}_{0.55}\text{N}_{0.01}$	6.34
400°C	1 h	54.9	5.0	36.1	0.94	0.12	$\text{CH}_{1.10}\text{O}_{0.49}\text{N}_{0.01}$	6.69
	2 h	56.0	5.3	35.1	0.76	0.12	$\text{CH}_{1.13}\text{O}_{0.47}\text{N}_{0.01}$	6.94
	3 h	59.6	4.7	31.3	1.00	0.14	$\text{CH}_{0.94}\text{O}_{0.39}\text{N}_{0.01}$	7.36

Source: DATA source: Sadaka et al., 2014 Energies. 7, 548–567.

The composition of the char varies with temperature and residence time as well during the pyrolysis. Table 16.11 shows that as the pyrolysis time increases from 1 hour to 3 hours, the concentration carbon increases in the char. As the pyrolysis temperature is increased, there is a marked increase in the carbon concentration in the char and a decrease in the concentrations of hydrogen and oxygen. Fig. 16.18 shows that the stoichiometry of the (residue) solid material after pyrolysis of biomass is close to that of coal as pyrolysis temperature and residence time increased.

16.10.2 Coke and charcoal

Once the volatile products have been pyrolyzed, one is left with a material that is mostly carbon, and the residual solid is called coke (from coal or wood) and charcoal (from slow pyrolysis of wood). Coke was of course used in blast furnaces to make iron (the volatiles would make the process less reproducible in reducing Fe_2O_3) by our ancestors, while charcoal was used in soap (mainly the alkalis in the ash) and as an adsorbent.

Coke and charcoal are highly porous, coke forms from wood with the holes left behind when the volatile components evaporate, and charcoal remains from the cellular framework of wood fibers. Addition of limited air in pyrolysis produces more volatile products and makes a more porous carbon residue. Active carbon is made this way.

These carbon residues then can be burned with air in the second stage of combustion. There are two modes of carbon combustion, with and without flames. If there is no flame over the carbon, then reaction occurs by surface reaction. There are multiple steps for the surface reaction: mass transfer of oxygen to the surface, (dissociative) adsorption of oxygen on

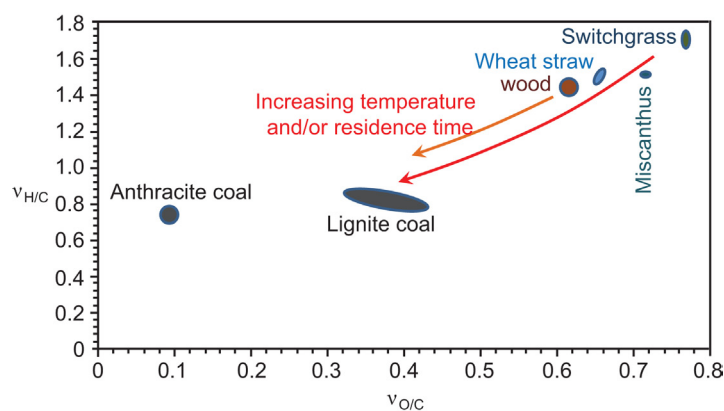


FIGURE 16.18 The stoichiometry or Roels' formula of the solid material, $\text{CH}_{v_{H/C}}\text{O}_{v_{O/C}}$, for different materials. The composition of the solid char residue of biomass after pyrolysis is close to that of coal.

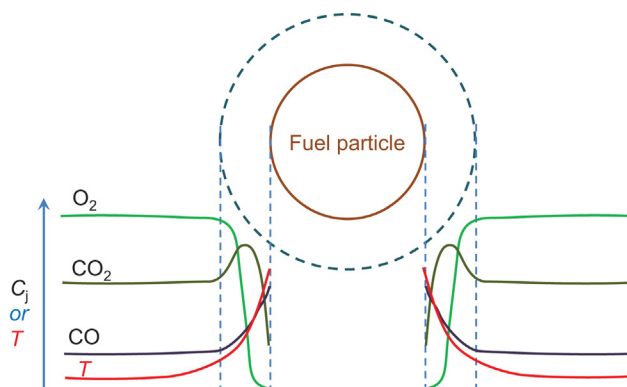


FIGURE 16.19 Concentration profiles around a burning carbon particle, rendering a homogeneous reaction in the boundary layer around the particle.

the carbon active centers (C_σ), reaction or transformation to form a CO or CO_2 molecule, and release of the gas molecule into the surroundings (exposing carbon active centers from below).



or to CO_2



if the reaction is deficient in O_2 . When there is a flame, burning is by both surface and homogeneous reactions. The surface reaction is primarily (16.49) and the homogeneous reaction is primarily



although this is in fact a free-radical chain reaction with many steps.

This creates a reacting boundary layer over the coke or charcoal particle with reactant and product composition profiles as illustrated in Fig. 16.19.

There is therefore typically a progression of burning of solids involving first a homogeneous reaction, where volatile gases are driven off and burn, followed by a homogeneous-heterogeneous reaction, where both homogeneous and surface reactions occur in a boundary layer, followed by a surface reaction, where glowing coals react only on the surface.

16.10.3 The campfire or charcoal grill

Almost everyone has seen a campfire or charcoal grill. When a log is placed in a campfire, it first sputters and pops as water trapped within the solid is released as the temperature rises, and then flames are observed around it (flame jets form as the organics escape from cracks in the log) but the surface remains dark. Then after most of these organics have escaped, the wood surface begins to glow as the surface reaction begins with the flame continuing. Finally, after the fire has “died down”, one observes no flame at all but just the glowing embers due only to surface reaction. Stirring the coals or blowing on the fire causes the flame to reignite for a while until it returns to the pure surface reaction mode. Finally, the heat release is too small to sustain reaction or the wood turns completely to ashes.

The burning process as one can observe from a campfire or charcoal grill is a perfect example of the pyrolysis, combustion and/or gasification. In order for the reactions to occur, high temperature is needed. Burning provides heat to raise the “solid fuel” temperature. While energy is needed to raise system temperature, pyrolysis and gasification processes are usually desired to keep more energy content in the final product (solid, liquid, or gases).

16.10.4 Solid wood or coal combustion

While less common today, solid wood and/or coal was the fuel for home heating prior to 1960's. Today wood and coal are burned in electric power plants, where fast and efficient combustion is desired. Therefore, coal plants grind large coal

chunks into fine powder and then blow it with air into burner jets, where it reacts with O_2 first by pyrolysis, and then the remaining coke burns, leaving behind an ash, which is a few percent of the weight of the original coal.

Most of us have never seen the inside of a coal-fired boiler, but the sparks rising from a campfire are very similar to the second stage of a coal-burning process. When a campfire is stirred, small particles of charcoal are broken off the log, and buoyancy carries them upward. They glow brightly by the heat released by heterogeneous carbon oxidation for several seconds until the carbon is all consumed.

In these processes the reactant O_2 flux is mass transfer limited around the reacting solid sphere, and the temperature of the particle is determined by heat transfer around the sphere, as shown in Fig. 16.16.

Example 16.1

Most of us have poked a campfire or sat by a fireplace at night and watched the sparks fly up. They glow a bright red, which indicates that they are emitting blackbody radiation from a source with a surface temperature of 1000–1200°C. You have also noticed that their color does not change until they suddenly disappear. The time for this reaction varies, but they seem to glow for a few sec and then suddenly disappear.

a. Estimate the temperature of a campfire spark.

b. How long does it take to consume a fiber bundle of $\phi 0.2\text{mm} \times 1\text{mm}$ pine wood fiber (particle)?

Solution

Let us construct mass and energy balances on the particle, which we assume to be a cylinder of dry pine wood particle of radius R . The reaction is



where X stands for the pine wood biomass (normalized by carbon), and ν_{HC} is the mole fraction of hydrogen over carbon in the biomass. The elemental composition of dry pine wood can be found in weight percent as C: 51.8%, H: 6.3 %, O: 41.3% and N: 0.1%. The lower heating value of dry pine wood is given by $-\Delta H_R = 21.03 \text{ MJ/kg}$.

Based on the elemental composition of pinewood, one can find the Roels' formula for pinewood as $CH_{1.4493}O_{0.5985}N_{0.1655}$. The lower heating value can be converted to the heat of reaction for (E16.1.1) as

$$-\Delta H_R = 1\text{kg} \times \frac{21.03 \text{ MJ/kg}}{0.518 + 12.011 \text{ kmol-C}} = 487.6 \text{ kJ/mol-C} \quad (E16.1.2)$$

The degree of reduction for pine wood is given by

$$\gamma_{DR} = 4\nu_C + \nu_H - 2\nu_O = 4 + 1.4493 - 2 \times 0.5985 = 4.2523 \quad (E16.1.3)$$

Thus, the heat of reaction for (E16.1.1) can be determined as

$$-\Delta H_R = \frac{487.6 \text{ kJ/mol-C}}{4.2523 \text{ mol-electron/mol-C}} = 458.7 \text{ kJ/mol-}O_2 \quad (E16.1.4)$$

We do not know, nor do we need, the exact kinetics of the reaction explicitly. It is a surface reaction between the biomass (carbon and hydrogen) on the surface of the particle and O_2 from the air.

A mass balance on O_2 around the particle yields

$$-r''_{O_2} A \left\{ \begin{aligned} &= -\frac{\gamma_{DR}}{4} r''_X A = -\frac{\gamma_{DR}}{4} \frac{dn_X}{dt} = -\frac{\gamma_{DR}}{4} \frac{2\pi R L \rho_X}{M_X} \frac{dR}{dt} \\ &= \bar{N}_{O_2} A = 2\pi R L k_c (C_{O_2,b} - C_{O_2}) \end{aligned} \right. \quad (E16.1.5)$$

where r'' is the rate of reaction based on the surface area. We have simply equated the rate of reaction of O_2 at its surface with the loss of moles of biomass particle, and the rate of mass transfer of O_2 to the surface.

An energy balance on the particle yields

Heat released due to reaction = heat lost by conduction + heat lost by radiation

$$(-r''_{O_2} A)(-\Delta H_R) = hA(T_s - T_a) + A\epsilon\sigma(T_s^4 - T_a^4) \quad (E16.1.6)$$

where all terms are familiar except the radiation term, with ϵ the emissivity of the surface, σ the Stefan-Boltzmann radiation constant, T_s , the carbon particle temperature, and T_a the ambient air temperature (300 K or whatever it was that night).

Combining Eqs. (E16.1.6) and (E16.1.5), one can obtain

$$h(T_s - T_a) + \epsilon\sigma(T_s^4 - T_a^4) = k_c(C_{O_2,b} - C_{O_2})(-\Delta H_R) \approx (-\Delta H_R)k_c C_{O_2,b} \quad (E16.1.7)$$

where we have assumed that $C_{O_2} \ll C_{O_2b}$, meaning that the oxidation of the carbon particle is mass transfer limited.

Now we need k_c and h , the mass and heat transfer coefficients around a cylinder. These come from Sherwood and Nusselt numbers, respectively, for flow around a cylinder,

$$Nu = 3.66 + \frac{0.085 Re Pr \frac{2R}{L}}{1 + 0.047 \left(Re Pr \frac{2R}{L} \right)^{\frac{2}{3}}} \quad (E16.1.8)$$

$$Sh = 3.66 + 1.077 \left(Re Pr \frac{2R}{L} \right)^{\frac{1}{3}} \quad (E16.1.9)$$

Since the fluid (air) is nearly stagnant, $Sh = Nu = 3.66$. Therefore, we have

$$Sh = \frac{k_c 2R}{D_{O_2-Air}} = 3.66 = \frac{h 2R}{k_T} = Nu \quad (E16.1.10)$$

where D_{O_2-Air} is the diffusivity of O_2 in air at atmospheric pressure, $D_{O_2} = 0.1 \text{ cm}^2/\text{s}$, and k_T is the thermal conductivity of air at atmospheric pressure, $k_T = 0.026 \text{ W/(m}\cdot\text{K)}$. As the wood particles burns, and the surface carbonize and thus one can assume black body radiation, that is, $\epsilon \approx 1$ and $\sigma = 5.6703 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$.

We can now solve our problem by substituting the parameters into Eq. (E16.1.7).

$$3.66 \frac{k_T}{2R} (T_s - T_a) + \epsilon \sigma (T_s^4 - T_a^4) = (-\Delta H_R) \times 3.66 \frac{D_{O_2-Air}}{2R} C_{O_2b} \quad (E16.1.11)$$

or

$$3.66 \frac{0.026}{0.2 \times 10^{-3}} (T_s - 300) + 5.6703 \times 10^{-8} (T_s^4 - 300^4) = 458.7 \times 10^3 \times 3.66 \frac{0.1 \times 10^{-4}}{0.2 \times 10^{-3}} \times \frac{0.21}{22.4 \times 10^{-3}} \quad (E16.1.12)$$

Which can be solved to give

$$T_s \approx 1441 \text{ K} = 1168^\circ\text{C}$$

which is in good agreement with the observed temperature of a spark (bright yellow). In this calculation we used for the concentration of O_2 in air the approximation

$$C_{O_2b} = \frac{0.21 \text{ mol}}{22.4 \text{ L}} \quad (E16.1.13)$$

Finally we return to the mass balance to calculate the time needed to burn completely the particle. Eq. (E16.1.5) can be reduced to

$$-\frac{\gamma_{DR}}{4} \frac{2\pi R L \rho_X}{M_X} \frac{dR}{dt} = 2\pi R L k_c (C_{O_2b} - C_{O_2}) \quad (E16.1.14)$$

or

$$-\frac{\gamma_{DR}}{4} \frac{\rho_X}{M_X} \frac{dR}{dt} = 3.66 \frac{D_{O_2-Air}}{2R} C_{O_2b} \quad (E16.1.15)$$

Separation of variables (R and t) gives

$$\frac{\rho_X \gamma_{DR}}{14.64 M_X D_{O_2-Air} C_{O_2b}} 2R dR = dt \quad (E16.1.16)$$

This equation can be integrated to yield

$$t = \frac{\rho_X \gamma_{DR} R_0^2}{14.64 M_X D_{O_2-Air} C_{O_2b}} \quad (E16.1.17)$$

Inserting the numbers ($\rho_X = 550 \text{ kg/m}^3$, $D_{O_2-Air} = 0.1 \times 10^{-4} \text{ m}^2/\text{s}$, and $M_X = 12.011 + 1.4493 \times 1.0079 + 0.5985 \times 15.9994 + 0.1655 \times 14.01 = 25.366 \text{ g/mol}$), we have

$$t = \frac{4.2523 \times 550 \times (0.1 \times 10^{-3})^2}{14.64 \times 25.366 \times 0.1 \times 10^{-4} \times 0.21 / 22.4} \text{ s} = 0.672 \text{ s} \quad (E16.1.18)$$

which is a reasonable time for a spark to disappear.

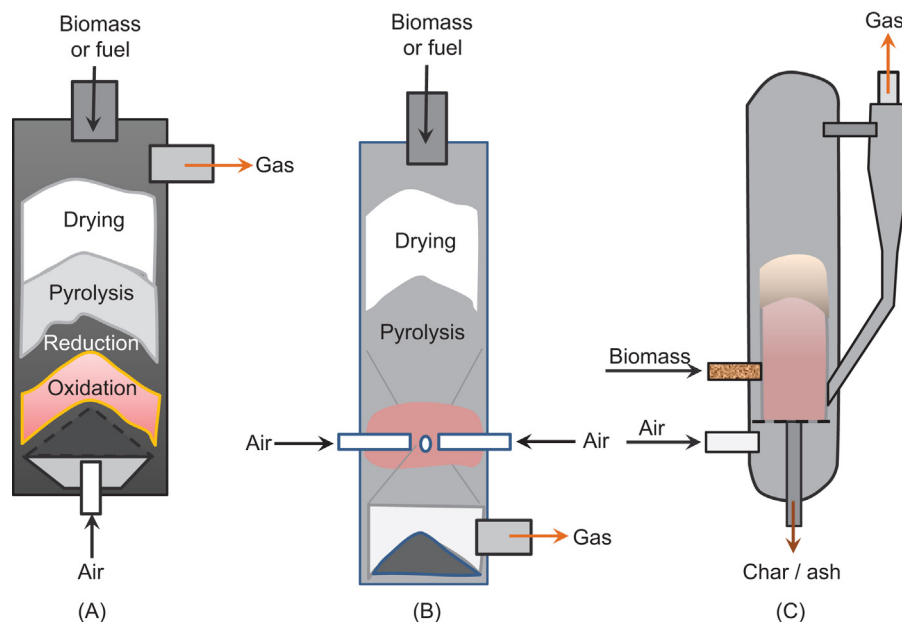


FIGURE 16.20 Schematics of gasification reactors. The major steps involved in gasification of biomass are drying or torrefaction, pyrolysis and oxidation. (A) Updraft. (B) Downdraft. (C) Fluidized bed.

16.10.5 Gasification and Fisher-Tropsch technology

Burning or combustion can produce maximum amount of heat if CO_2 and H_2O are the only products for carbon and hydrogen in the solid fuel. In some applications, we seek to render solid fuel to easily transportable gas mixtures retaining the majority of the energy value. Coal gasification and liquefaction were evaluated in the twentieth century especially during the petroleum crises. Biomass gasification is gaining prominence in the twenty-first century.

Gasification is a versatile technique for coal and/or biomass conversion. Gasification of biomass is usually carried out between 700°C and 1200°C in a fraction of a second. Fig. 16.20 shows schematics of typical gasification reactors. During the gasification process, the biomass undergoes drying / torrefaction and pyrolysis before gasification (oxidation of the carbonized materials). The principles of these processes have been discussed earlier in this section. The process can be semi-batch as shown in (a) updraft and (b) downdraft reactors, or continuous as shown in (c) fluidized bed gasifiers.

The importance of gasification in a future economy lies on its potential to facilitate the use of biomass in the existing petroleum based industry. Fig. 16.21 shows some of the commodity chemicals can be produced through gasification of woody biomass. Besides these catalytic routes, syngas has been subjected to bioconversion as well. Certain bacteria, or enzymes can be applied to convert syngas to chemicals similar to sugars. Therefore, gasification has been a well-studied method in thermochemical conversions. However, as expected, the bioconversion efficiency is much lower for gaseous substrates than solid / liquid substrates.

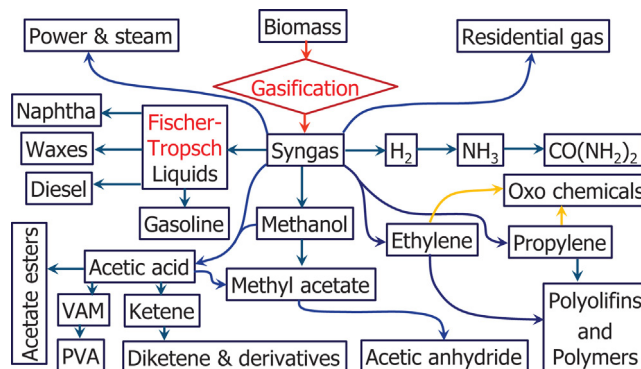


FIGURE 16.21 The catalytic routes to commodity chemicals from biomass via gasification.

TABLE 16.12 Typical compositions in syngas from gasification of woody biomass.

Heat source	Autothermal	Allothermal	
Gasifying agent	Air	O ₂ + Steam	Steam
H ₂ , %	11 – 16	23 – 28	35 – 40
CO, %	13 – 18	45 – 55	22 – 25
CO ₂ , %	12 – 16	10 – 15	20 – 25
CH ₄ , %	2 – 6	< 1	9 – 11
N ₂ , %	45 – 60	< 5	< 1
LHV, MJ/Nm ³	4 – 6	10 – 12	12 – 14

Table 16.12 shows the typical compositions of gases in the syngas as a function of the oxygen addition. In anaerobic conditions, the gasification process is endothermic. Large amount of heat is needed to maintain the high temperature (700°C – 1000°C) as well as to provide energy for breaking the polymer binds. The benefit of anaerobic gasification is the high heating (or energy) value of syngas. Table 16.12 shows that the low heating value (LHV) of syngas produced with steam as heating medium is 12–14 MJ/Nm³, while it is only 4–6 MJ/Nm³ for syngas produced by partial burning with air. The high-energy content in the syngas is desirable.

The energy requirement of gasification can be satisfied by adding oxygen in the feed. When oxygen is available, biomass will burn or partially burn to provide energy to the system. However, the burning of biomass will reduce the energy content in the final product gas stream. Therefore, oxygen content should be controlled at low level, just enough to provide heat to maintain the desired gasification temperature.

Gasification is a process in which the carbon and hydrogen raw material sources are first converted to basic building block chemicals: CO and H₂ and polymerize together to produce desired products, such as alkene:



This process was discovered and developed primarily in Germany during World Wars I and II to provide synthetic liquid fuels to compensate for the Allies blockade of crude oil shipment. (The argument can be made that both world wars were essentially fought over access to petroleum in the Caucasus region of Russia and the Middle East. The US blockade of Japanese access to Far East crude oil was a major factor in Japan declaring war on the United States with the bombing of Pearl Harbor. These arguments are summarized in the book *The Prize* by Daniel Yergin).

Fisher-Tropsch (FT) technology has been practiced on a large scale in South Africa because of the need for an independent source of liquid fuels during their political isolation, and they had abundant coal to make syngas. However, these processes are potentially an exceedingly important replacement for liquid fuels to use when crude oil supplies are depleted. Using coal (several hundred years supply in the United States alone) and natural gas (more proven reserves than petroleum), we can be assured of sources of liquid fuels for transportation through this technology long after supplies of crude oil and even natural gas have been used up. The more prominent use of Fisher-Tropsch technology is the renewable biomass feedstock, as petroleum, natural gas, and coal will eventually be depleted. Biomass as we know it is renewable and will not be depleted as long as the Sun is sending out rays.

Fisher and Tropsch found that when a mixture of CO and H₂ was heated to about 250°C at high pressures over an iron catalyst, polymer would form, and under suitable conditions this had the appropriate molecular weight for gasoline and diesel fuel. Different metal catalysts give different molecular weights (Ni produces CH₄) and different amounts of alkanes (Fe and Re), olefins (Ru), and alcohols (Rh); so catalysts and process conditions can be altered to produce a desired molecular weight and distribution.

The products are essentially all linear molecules, which for olefins and alcohols have the double bond or the OH group on the end carbon (α -olefins and α -alcohols). The mechanism of this polymerization process is thought to be similar to (but also very different from) Ziegler Natta (ZN) polymerization of ethylene and propylene on Ti. It is thought that CO adsorbs and hydrogenates (perhaps to form the CH₂ group) on an adsorption site adjacent to an adsorbed alkyl R, as shown in Fig. 16.22. If the CH₂ inserts between the metal and the adsorbed R, an adsorbed RCH₂- is obtained, which can add another CH₂ to form RCH₂CH₂-, and the chain repeats itself indefinitely until the adsorbed alkyl dehydrogenates to olefin, hydrogenates to paraffin, or hydrates to α -alcohol.

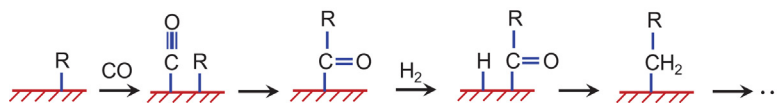


FIGURE 16.22 Proposed mechanism for Fischer-Tropsch polymerization of CO and H_2 to form alkane polymer.

The CO and H_2 (syngas) for FT synthesis were initially made by the gasification of coal, which was plentiful in Germany. Fig. 16.23 shows the equilibrium compositions for the gasification of carbon as a function of temperature. One can observe that the gas mixture consists of mostly CO and H_2 at high temperatures (greater than $900^\circ C$). At lower temperatures, equilibrium favors the formation of CO_2 and CH_4 in the gas mixture instead of H_2O .

Besides coal and biomass, syngas can also be made using naphtha or other hydrocarbon feedstocks, such as the methane from natural gas,



Note that coal produces CO and H_2 in a 1:1 ratio, naphtha in a 1:2 ratio, and methane in a 1:3 ratio. Because of the need in thermal energy to shift the reactions forward, oxygen (or air) is usually supplied to partially oxidize the carbon (and hydrogen) to maintain energy balance. An excess of H_2 is thus usually desired; so alkanes are the preferred feedstock.

Existing syngas plants operate by direct oxidation of natural gas



using pure O_2 from a liquid air plant. This process, called autothermal reforming, uses this exothermic reaction in an adiabatic reactor and produces the 1:2 ratio of $CO:H_2$ that is ideal for methanol or FT processes.

Today, more attention is paid to the gasification of renewable biomass. The energetics in gasification of coal and lignocellulosic biomass are similar on the same carbon mass basis. Another feedstock of interest is the black liquor in a chemical pulp mill. Currently, the black liquor is being burned to recover the pulping chemicals and thermal energy that is needed in the pulp and paper making processes. The black liquor gasification is therefore not going to make a significant contribution to our needs in liquid fuel or hydrocarbon, but it can improve the pulp mill energy efficiency.

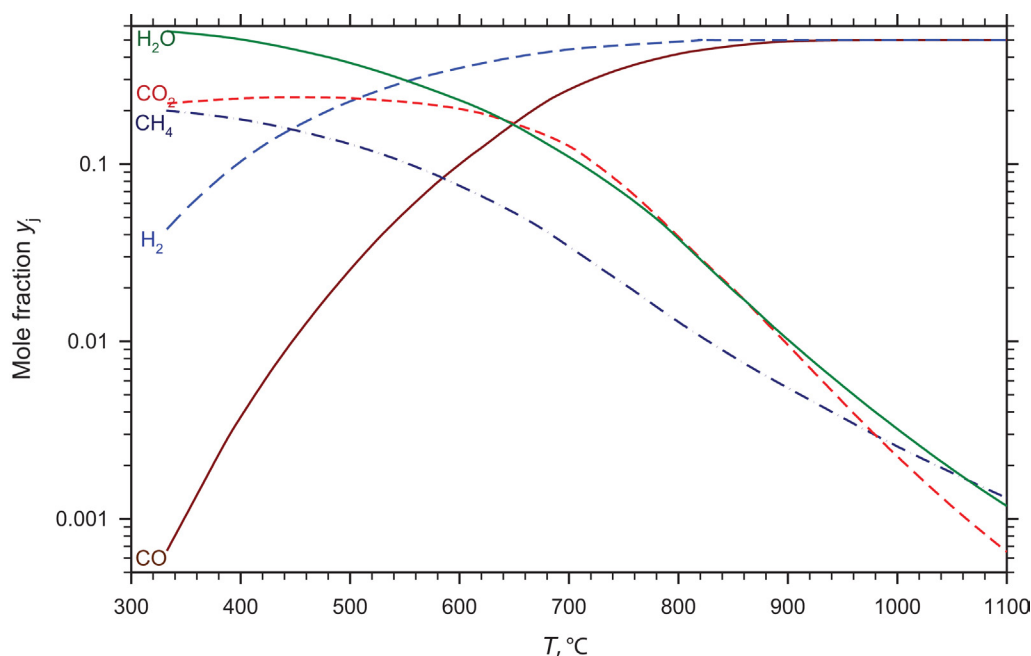


FIGURE 16.23 Equilibrium mole fractions for the carbon-steam reaction as a function of temperature.

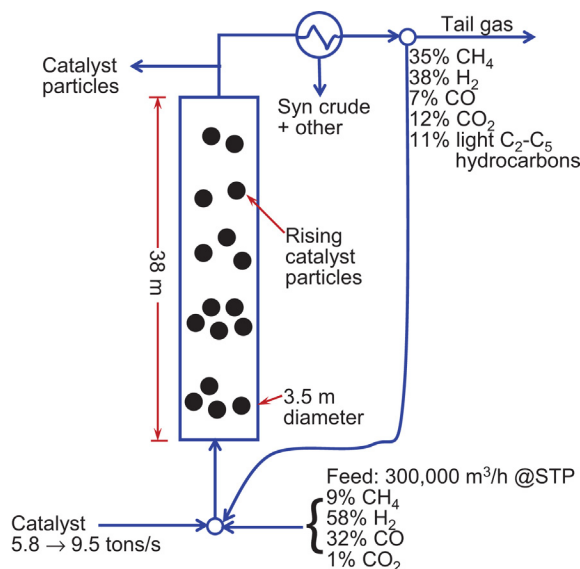


FIGURE 16.24 Schematic of Sasol Fischer-Tropsch process.

In gasification, O_2 is usually added for energetics reasons, as shown in Table 16.12. The gasification reactions without oxygen are endothermic, requiring energy to complete. Partially burning H_2 to H_2O or CO to CO_2 can produce the heat needed for the reactions to complete. To increase the availability of H_2 , the steam shift reaction,



can be carried out.

Gasification is employed today, for example, in ammonia production. Ammonia has wide applications. It is a precursor for urea, a commonly used fertilizer in agriculture. The ammonia synthesis reactions will be discussed in Chapter 8 (Section 8.3). The hydrogen gas is provided by gasification.

This FT process together with gasification may one day be the dominant method by which we will obtain some of our liquid fuels from renewable biomass, and coal. This technology is capable of supplying at least 200 years of liquid hydrocarbons at current consumption rates from known proven reserves of coal. The biomass as renewable resources, on the other hand, can supply our needs for liquid fuel “indefinitely.”

Two types of reactors will be discussed, a *straight-through transport reactor*, which is also referred to as a *riser* or *circulating fluidized bed*, and a *packed-bed reactor* (PBR), which is also referred to as a *fixed-bed reactor*.

Riser. Because the catalyst used in the process decays rapidly at high temperatures (e.g., $350^\circ C$), a *straight-through transport reactor* is used. This type of reactor is also called a *riser* and/or a *circulating bed*. A schematic diagram is shown in Fig. 16.24. Here the catalyst particles are fed to the bottom of the reactor and are shot up through the reactor together with the entering reactant gas mixture and then separated from the gas in a settling hopper. The volumetric gas feed rate is at $3 \times 10^5 \text{ m}^3/\text{h}$.

A schematic of an industrial *straight-through transport reactor* used at Sasol are shown in Fig. 16.25 together with the composition of the feed and product streams. The products that are condensed out of the product stream before the stream is recycled include Synoil (a synthetic crude), water, methyl ethyl ketone (MEK), alcohols, acids, and aldehydes. The reactor is operated at 25 atm and $350^\circ C$ and at any one time contains 150 tons of catalyst. The catalyst feed rate is 6 to 9.5 tons/s, and the gas recycle ratio is 2:1.

Packed bed. The packed-bed reactor used at the Sasol plant to carry out Fischer-Tropsch synthesis reaction is fed at a syn-gas rate of $30,000 \text{ m}^3/\text{h}$ (STP) at $240^\circ C$ and 27 atm. The reactor contains 2050 tubes, each of which is 5.0 cm in diameter and 12 m in length. The iron-based catalyst that fills these tubes usually contains K_2O and SiO_2 and has a specific area on the order of $200 \text{ m}^2/\text{g}$. The reaction products are light hydrocarbons along with a wax that is used in candles and printing inks. Approximately 50% conversion of the reactant is achieved in the reactor.

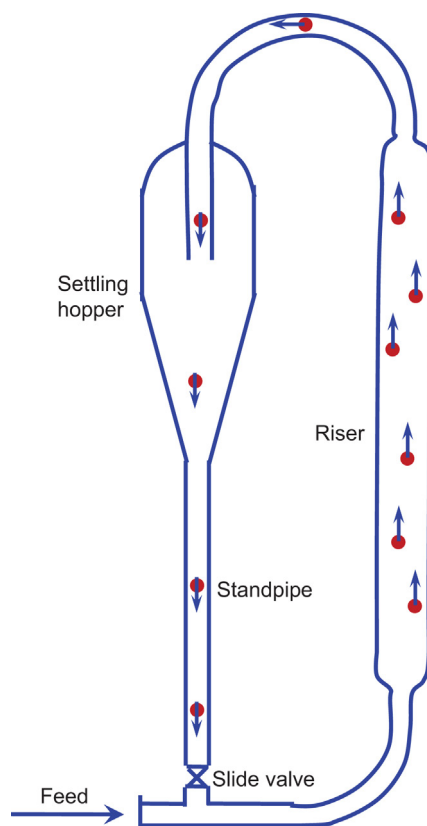


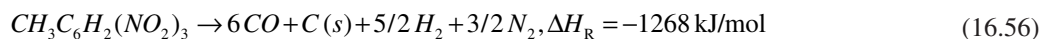
FIGURE 16.25 A schematic of reactor system, where the detailed flow of the riser is shown in Fig. 16.24.

16.11 Solid and liquid explosives

In combustion of solids such as charcoal, a reaction occurs between carbon and O_2 from the air in diffusion-limited reactions. In the year AD 142, a Chinese named Boyang Wei wrote that when charcoal was combined with sulfur and potassium nitrate (obtained by crystallizing liquid animal wastes in a process too messy to describe), the mixture of solids when ignited had quite different characteristics. This mixture would fizz with a flash of light. Thus were born explosives, which Westerners were the first to turn into materials of warfare in the fifteenth century.

As mentioned previously, the animal waste sources of fixed nitrogen were too limited for conducting a large-scale war, and chemical engineers developed the Haber process for making ammonia from N_2 and the Ostwald process to oxidize NH_3 into NO and thus to HNO_3 . The explosives business then evolved through nitroglycerine, nitrocellulose, and TNT to the modern plastic explosives and rocket fuels.

A solid or liquid explosive is simply a chemical or a mixture of solids that contains fuel and oxygen in the condensed state so that no diffusion processes slow the rate. The reaction of TNT can be written approximately as



which produces a lot of heat and gases. There is not enough oxygen in the molecule to convert all C to CO_2 or H to H_2O , but the products quickly are heated to sufficient temperatures that they react instantly with O_2 at contact.

If the solid is in an open container, the reaction just fizzes, but if it is confined long enough to build up pressure, it generates a pressure wave, which causes accelerated propagation of the combustion wave, which is heard as a bang. If the container is confined on all but one side (the nozzle), reaction creates a rocket.

The art and engineering of propellant and explosive manufacture consists in finding suitable combinations and treatments of solids that will produce a “stable” compound that will not ignite until desired and will then burn with the appropriate rate to produce the desired blast wave or thrust. Obviously these are dangerous experiments, and they should be attempted after one figures out all the possibilities and what to do about them.

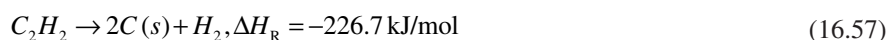
Since an explosive solid contains fuel and oxidant in close proximity, the exothermic reaction can occur very quickly and without diffusion control, just as for separate fuel and oxidant systems. Premixed flames and explosions with gases in-

TABLE 16.13 Heats of formation of hydrocarbons

C_2H_6	-84.68 kJ/mol
C_2H_4	+52.30
C_2H_2	+226.7
$C = C - C = C$	+110.2
$C = C - C \equiv C$ (VAc)	+304.6

volve the same basic idea with both fuel and oxidant mixed before reaction begins (and potentially disastrous consequences if they are ignited with inappropriate mixtures and confinement).

Another potentially explosive class of compounds is multiply bonded hydrocarbons. Early in the twentieth century, chemical engineers learned by disastrous accidents that pure acetylene itself can detonate because the reaction



is highly exothermic. Many acetylene tanks and pipes exploded before we learned to add stabilizers (chemicals such as acetone, which scavenge free radicals, which would otherwise promote chain-branching reactions). Even then, acetylene is sufficiently dangerous that it is seldom used in large quantities in the chemical industry.

Acetylene is widely sold as the fuel for welding torches, and it is stored in large cylinders at high pressures in many welding shops. In fact, this acetylene is mixed with acetone, which has been found to be an effective scavenger of acetylene decomposition, so that these tanks are relatively safe.

Table 16.13 lists the heats of formation of several of these potentially dangerous hydrocarbons.

16.12 Explosions and detonations

In the previous section we described one type of reaction that can cause an explosion, namely, the situation where fuel and oxidant are mixed in solids or liquids that can release large amounts of energy very quickly. These processes can also occur in premixed gases.

An example of useful explosions in gases is the repeated explosions that occur in the automobile engine. However, most examples of explosions in gases are in fact disasters in which products burst walls of containers and cause havoc.

An explosion can be defined as a fast, transient, exothermic reaction. It needs exothermicity to generate energy and must be fast to generate this energy very quickly in a transient pulse. We can also distinguish between events in which the reaction propagates at subsonic velocity as an explosion and one in which the reaction propagates with sonic or supersonic velocity as a detonation.

In practice, we call an explosion a reaction that makes noise. This can be a “whoosh,” a “thump,” or a “bang” in order of increasing rate of energy release and time of confinement. The bang is caused by a buildup of pressure that is released very quickly as the confinement system ruptures or the reactor ruptures. The parameter that distinguishes these characteristics is the flame velocity u_F , which is the velocity with which the reaction front propagates down a tube or across a container. The velocity of sound in air at 300 K is approximately 1100 ft/s or 300 m/s. If the velocity of propagation is less than the velocity of sound, the wave is called a deflagration, and if it is at or above the velocity of sound, it is called a detonation. Detonation can do much more damage because of the shock wave. We call a subsonic reaction wave a deflagration and a supersonic wave a detonation.

If CH_4 and air at the stoichiometric ratio (9.5% CH_4 in air) at atmospheric pressure are ignited at one end of a pipe, the pressure will ultimately rise by a factor of ~ 10 , and this pressure wave will travel at 300 m/s down the pipe. The heat of reaction is -803 kJ/mol of CH_4 , and all this heat will be released and the pressure will rise very quickly.

Explosions in solids and liquids can be even more violent than in gases because the energy content per mole is comparable, but the density of solids and liquids is approximately 1000 times the density of gases at atmospheric pressure. As such, accumulation of dust in grain storage, grain processing facilities and metal processing facilities can lead to spectacular explosions that are very dangerous.

These considerations in fact underestimate the damage an explosion can cause as the flame speed becomes sonic and generates a shock wave. The pressure wave travels so fast that it carries considerable momentum, and this can burst walls even more effectively than a static calculation of wall strength would indicate. Sonic waves also reflect and focus their energy, so that quite unpredictable and extreme localized damage can occur from an explosion.

TABLE 16.14 Some famous accidents in the chemical industry.

Accident	Year	Fatalities	Reaction or key reactant(s)
The Texas City Disaster, Port of Texas City Explosion of fertilizer on board <i>SS Grandcamp</i> liberty ship.	1947	581	NH_4NO_3 explosion
The Texas City Disaster II Union Carbide corporation chemical plant	1969	0	vinylacetylene explosion
Flixborough Disaster, England The chemical works, owned by Nypro UK	1974	28	cyclohexane VCE
Seveso disaster, Milan, Italy A small chemical plant of ICMESA (<i>Industria Chimica Meda Società Azionaria</i>), a subsidiary of Givaudan, Hoffmann-La Roche (Roche Group), located at Meda, Italy	1976	0	2,4,5-trichlorophenol to TCDD
Bhopal Disaster Union Carbide India pesticide plant, Bhopal, India	1984	~2500	methylisocyanate hydrolysis
Norco, Louisiana, Oil Refinery Explosion Shell plant explosion is Diamond, Louisiana	1988	7	Hydrocarbon vapor
Phillips polyethylene, Pasadena, Texas The Houston Chemical Complex (HCC) facility, Phillips.	1989	23	Ethylene, isobutene VCE
Texas City Refinery Explosion BP's Texas City Refinery	2005	15	Pentanes, hexanes
Georgia Sugar Refinery Explosion Imperial Sugar, Port Wentworth, Georgia	2008	14	Dust explosion
West Fertilizer Company Explosion, Texas	2013	15	NH_4NO_3 explosion
Tianjing port explosions Tianjing port warehouse for hazardous goods, China	2015	173	Nitrocellulose, NH_4NO_3 , KNO_3 , CaC_2 , NaCN , ...
Explosion at the Petroquímica Mexicana de Vinilo SA de CV plant in Coatzacoalcas, Veracruz, Mexico	2016	32	Ethylene, vinyl chloride
"7.12" Explosion at Yibin Hengda Technology, Sichuan, China	2018	19	Unlabeled Sodium Chlorate
"11.28" Zhangjiakou Loading Trucks Explosion, Hebei Shenghua Chemical Co. Ltd, Hebei, China	2018	24	Vinyl chloride (leaked out from plant)
University Waste Treatment Lab Explosion, Beijing Jiaotong University, Beijing, China	2018	3	H_2 from Magnesium reaction with Phosphoric Acid
Xiangshui Chemical Plant Explosion at the Tianjiayi Chemical Co., Ltd., Yancheng, Jiansu, China	2019	78	Phenylenediamine
Explosion at the Industrias Químicas del Oxido de Etilenol in Tarragona, Catalonia, Spain	2020	2	Ethylene Oxide

16.13 Reactor safety

The chemical industry is one of the safest industries in the United States in terms of accidents and fatalities, with approximately 10 fatalities per year for 100,000 workers. Your chances of getting killed in driving to and from work are much higher than while at work in the most hazardous job you could have in the chemical industry.

Nevertheless, accidents in chemical industry can be spectacular, with great potential for loss of life and income for many people. Most importantly, chemical engineers (you) will be responsible for creating safe processes and protecting the lives and health of your colleagues.

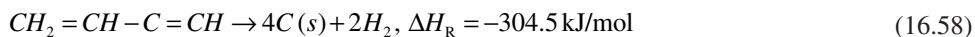
A great deal can and should be said about safety, but we have only been able to outline the principles by which chemical reactors may go out of control. We will conclude our discussion of safety by listing some of the notorious accidents that have occurred in the chemical industry (see Table 16.14).

The Texas City Disaster was perhaps the first "modern" chemical disaster, and it is still the US chemical accident with the most casualties. It occurred when a barge of ammonium nitrate (NH_4NO_3 or AN) fertilizer was being unloaded in Galveston Bay near Texas City. A fire started in the crew quarters of the barge. The fire department was spraying water on the fire, and many people on the shore were watching the action. The latest explosion involved with AN was in West, Texas, in 2013.

Suddenly the barge exploded, taking with it a sister barge, a sulfur plant on the shore, and two airplanes flying overhead. No one expected this disaster, and all procedures were being followed according to the “standard safety practices” of 1947. AN was a fertilizer, not an explosive! No one had “done the experiment” until the fire happened to get hot enough with a large enough quantity of AN to cause its detonation.

By current practice, large quantities of AN are never accumulated or exposed to heat or fires. However, fertilizer storage warehouses still explode occasionally, and AN has become a popular, inexpensive, and readily available material for terrorists, for example, in the World Trade Center bombing in New York City in 1992 and the Oklahoma City bombing of 1995.

A second explosion occurred in a chemical plant in Texas City, Texas, some years later, and this was called the Texas City Disaster II. This explosion occurred when a distillation column used to purify butadiene from other C4 hydrocarbons was operating improperly and the feed was shut off, as was the product stream from the reboiler. The column suddenly blew up, sending the column like a rocket — a mile into the town. After some investigation, it was surmised that the reboiler accumulated a high concentration of vinyl acetylene, which is a strongly endothermic compound. The initial explosion was the reaction



The hydrogen pressure burst the reboiler and the contents of the column then ignited, turning the distillation column into a primitive but effective rocket that took off. Fortunately, no one was around at either the launch site or landing site. However, the town’s residents heard a loud bang, and they had been highly sensitized from the previous one when the AN barges blew up a few years before.

The third Texas City disaster came with the refinery explosion on March 23, 2005, when a hydrocarbon vapor cloud exploded at the isomerization process unit at BP’s Texas City refinery, killing 15 workers and injuring more than 170 others. The isomerization plant at the site was designed for the conversion of low octane hydrocarbons, through various chemical processes, into higher octane rating hydrocarbons that could then be blended into unleaded petrol. The leakage of large quantity of hydrocarbon into the air caused explosion.

Yes. Sugars can explode. The 2008 Georgia sugar refinery explosion was an industrial disaster that occurred on February 7, 2008 in Port Wentworth, Georgia. Fourteen people were killed and 42 injured when a dust explosion occurred at a sugar refinery owned by Imperial Sugar.

Flixborough, the Phillips polyethylene plant explosion, Norco Shell refinery explosion and the Texas City refinery explosion were vapor cloud explosions (VCE) of hydrocarbons that escaped through leaks in chemical reactors. In Flixborough disaster near the village of Flixborough, North Lincolnshire, England, Nylon 6 was being made by oxidation of cyclohexane to produce caprolactam.

In the Phillips plant low-density polyethylene was being produced in a process that uses isobutane solvent at very high pressures. These liquids escaped and vaporized without combustion because no ignition sources were nearby. After the hydrocarbon vapors had spread large distances and had become diluted with air (O_2), a cigarette or pilot light somewhere ignited the premixed alkane—air mixture creating a VCE, with disastrous consequences to the plant, to the neighborhood, and in the latter case to people.

Bhopal, the site of the largest chemical accident in the past 50 years, wasn’t an explosion but rather an uncontrolled reaction. The plant in Bhopal, India, owned jointly by Union Carbide and the Indian government, was producing methyl isocyanate as an intermediate for a pesticide. Water was admitted into a storage tank containing this chemical, which caused it to hydrolyze and produce CO, HCN, and unreacted MIC, which spread downwind into a crowded slum nearby and caused many deaths and casualties. The desired reaction to synthesize MIC was



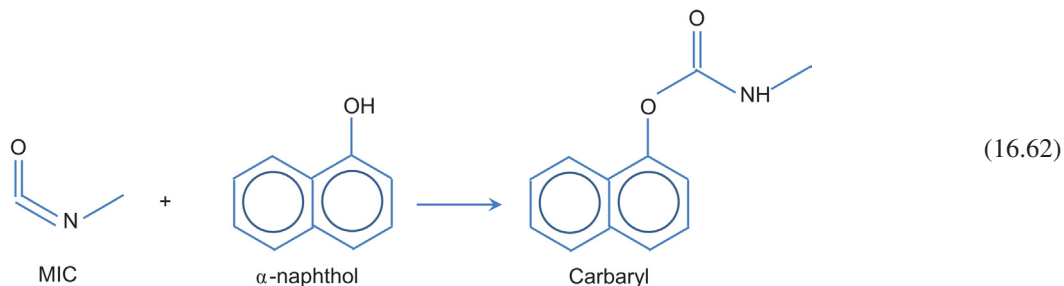
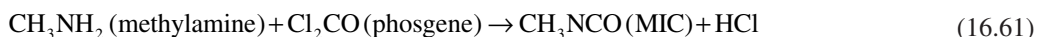
and the very undesired hydrolysis reactions were



all of which are highly toxic.

The Bhopal chemical plant was used to produce agricultural pesticides and herbicides. These chemicals are very important in agriculture to maintain insect and weed populations under control so that crop yields can be improved. One wants to produce pesticides and herbicides that are very selective in destroying a particular insect or plant but are not also toxic to other organisms (such as humans). Here the objectives are to produce a chemical that is toxic to specific plants or animals but not to others. Some desirable characteristic of these chemicals is that they (1) attack only the desired pests, (2) do not decompose during storage and shipment, and (3) decompose soon after application so that pesticide residues do not remain on food or contaminate ground water. It is obvious that considerable creative engineering goes into formulating and testing these agricultural products.

At Bhopal they were manufacturing SEVIN, also called carbaryl, a broad-spectrum insecticide that was and still is used on many crops in most countries throughout the world. The reaction steps to manufacture SEVIN are



In the reaction steps leading to SEVIN, a common agricultural pesticide, all of the reactants are quite inert and harmless except phosgene, MIC, and the final product.

Xiangshui chemical plant explosion, Yancheng Industrial Park, Jiangsu, China. The March 21, 2019 explosion occurred at a local time of 14:48 (06:48 GMT). 78 people were killed and at least 94 were severely injured, 32 of whom were critically injured. Around 640 people, included children at a local kindergarten, required hospital treatment and were taken to 16 hospitals.

The force of the blast started numerous fires in Yancheng, knocked down several buildings, and reportedly destroyed windows kilometers away. The fire was controlled by 03:00 local time next morning. Considerable damage was caused to nearby factories and offices; including the roof of Henglida Chemical Factory, 3 km from the explosion, fell in. At least one of the people killed was in another building destroyed by the blast. Windows are reported to have been blown out up to 6 km away from the explosion, and houses and other buildings were damaged in the nearby village-level administrative divisions. This explosion was so strong that it even registered on the earthquake sensors and the devastation could be seen by satellites. According to the South China Morning Post article entitled “Devastation at blast site after China chemical plant explosion leaves at least 64 dead, 640 injured” discusses the point of the surrounding three rivers were polluted with exceedingly levels of dichloroethane and dichloromethane by $2.8\times$ and $8.4\times$ the national water quality standards. The 170 m wide crater and 2 m deep required filling along with neutralizing the soil to prevent contamination to the surrounding community. “This chemical plant was flattened along with the surrounding 16 factories also have varying degrees of damage.”

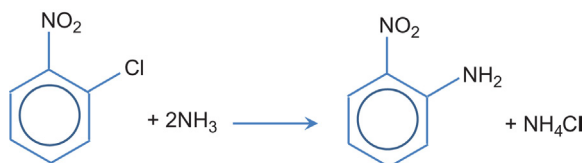
On April 4, 2019, the Standing Committee of the Yancheng Committee of the Communist Party of China had a meeting at which it was decided to definitively close down the Xiangshui Chemical Industry Park.

University lab can explode too. While the ferocity of an accident is proportional to the amount and concentration of the chemicals caused it, bad accidents can occur in a university lab. On the morning of December 26, 2018, a fire/explosion occurred at the waste treatment lab, Environmental Engineering Department of Beijing Jiaotong University in China. Three students died at the accident, where magnesium was mixed with phosphoric acid to prepare for the wastewater treatment of waste filtrate liquor. The hydrogen produced from the reaction vessel exploded due to the spark generated by the (mixer) shaft and motor.

Example 16.2 Reactor runaway

(This is a story retold based on Fogler, 1999).

An explosion occurred at Monsanto plant in Sauget, Illinois, on August 8, 1969 at 12:18 am. The blast was heard as far as 10 miles away and people were awakened from their sleep. The culprit was a batch reactor producing nitroaniline from ammonia and *o*-nitrochlorobenzene (ONCB):



The reaction is normally carried out at 175°C and about 500 psi. The ambient temperature of the cooling water in the heat exchanger is 25°C. The reactor temperature could be changed by adjusting the coolant rate. At the plant setting, the reactor tem-

perature could be maintained at 175°C at the maximum coolant rate if the ambient temperature of 25°C could be maintained throughout the heat exchange.

On the day of the accident, two changes in normal operation occurred:

1. The reactor was charged with 9.044 kmol of ONCB (nearly three times of the normal 3.17 kmol), 33.0 kmol of NH_3 (instead of 43 kmol in normal operations) and 103.7 kmol of H_2O (about the same as the normal of 103.6 kmol).
2. The reaction is normally carried out isothermally at 175°C over a 24-h period. Approximately 45 min after the reaction was started, cooling to the reactor was turned off for 10 min. It was not unusual not to cool in that 10 min or so on period when the normal charge of 3.17 kmol of ONCB was used and no ill effects occurred.

The reactor had a safety relief valve with a disk rupture pressure of about 700 psi. Once the disk ruptures, the water would vaporize, and the reaction would be cooled (quenched) by the release of the latent heat of vaporization.

Plot the temperature-time trajectory up to a period of 125 min after the reactants were mixed and brought up to 175°C. Show that the following three conditions had to have been present for the explosion to occur: (1) Increased ONCB charge; (2) Reactor cooling stopped for 10 min; and (3) relief system failure.

Additional information: The reaction rate is

$$-r_{\text{ONCB}} = k C_{\text{ONCB}} C_{\text{NH}_3}, \text{ with } k = 0.00017 \text{ m}^3 / (\text{kmol} \cdot \text{min}) \text{ at } 188^\circ\text{C}$$

The reactant volume for the charge of 9.044 kmol of ONCB is $3.265 \text{ m}^3 \text{ ONCB}/\text{NH}_3 + 1.854 \text{ m}^3 \text{ H}_2\text{O} = 5.119 \text{ m}^3$. The reactant volume for the charge of 3.17 kmol of ONCB is 3.26 m^3 . Thermodynamic and kinetic parameters are— $\Delta H_R = -5.9 \times 10^5 \text{ kcal/kmol-ONCB}$; $E_a = 11.273 \text{ kcal/mol}$; $C_{p,\text{ONCB}} = 40 \text{ cal}/(\text{mol} \cdot \text{K})$; $C_{p,\text{H}_2\text{O}} = 18 \text{ cal}/(\text{mol} \cdot \text{K})$; $C_{p,\text{NH}_3} = 8.38 \text{ cal}/(\text{mol} \cdot \text{K})$.

Assume $\Delta C_p = 0$, $UA_H = 35.85 \text{ kcal}/(\text{min} \cdot ^\circ\text{C})$ with $T_a = 298 \text{ K}$.

Solution

The stoichiometry of the reaction may be represented by



A sketch of a batch reactor is shown in Fig. E16.2.1. Mole balance of reaction mixture in the reactor as a whole leads to

$$r_A V = \frac{dn_A}{dt} \quad (\text{E16.2.2})$$

where

$$-r_A = k C_A C_B \quad (\text{E16.2.3})$$

and

$$C_A = C_{A0}(1 - f_A) \quad (\text{E16.2.4})$$

$$C_B = C_{B0} - 2C_{A0} f_A \quad (\text{E16.2.5})$$

$$k = 0.00017 \exp \left[\frac{11273}{1.987} \left(\frac{1}{188 + 273.15} - \frac{1}{T} \right) \right] \text{ m}^3 / (\text{kmol} \cdot \text{min}) \quad (\text{E16.2.6})$$

Thus, Eq (E16.2.2) can be reduced to

$$\frac{df_A}{dt} = k (1 - f_A) (C_{B0} - 2C_{A0} f_A) \quad (\text{E16.2.7})$$

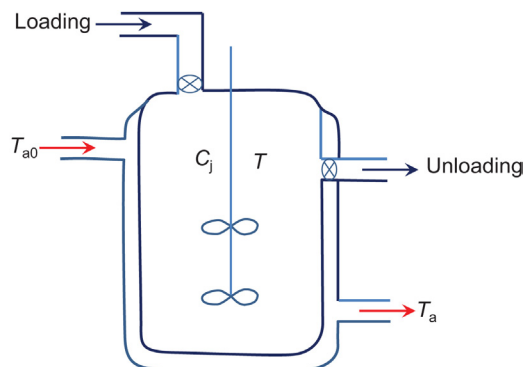


FIGURE E16.2.1 A schematic of a batch reactor system.

Energy balance over the reactor, for example, Eq. (16.7), leads to

$$\frac{dT}{dt} = \frac{UA_H(T_a - T) + r_A V \Delta H_R}{\sum n_j C_{Pj}} \quad (\text{E16.2.8})$$

The energy balance equation has the appearance of heat removal (due to heat transfer out of the reactor as removed by the cooling water) and heat generation as given by

$$H_R = UA_H(T - T_a) \quad (\text{E16.2.9})$$

$$H_G = (-r_A V)(-\Delta H_R) \quad (\text{E16.2.10})$$

Since $\sum v_j C_{Pj} = 0$, we have

$$\sum n_j C_{Pj} = \sum n_{j0} C_{Pj} = n_{A0} C_{PA} + n_{B0} C_{PB} + n_{W0} C_{PW} = 9.044 \times 40 + 103.7 \times 18 + 33 \times 8.38 \text{ kcal/K}$$

or $\sum n_j C_{Pj} = 2504.9 \text{ kcal/K}$

The behavior of the reactor can be simulated with Eqs. (E16.2.7) and (E16.2.8).

(a) Isothermal operation in the first 45 minutes

We first simulate the reaction isothermally at 175°C for the first 45 minutes until the time the cooling was turned off. For isothermal operations, the reaction rate coefficient is constant as it changes only with temperature as shown in Eq. (E16.2.6), $k = 0.0001167 \text{ m}^3/(\text{kmol} \cdot \text{min})$ at 175°C. Eq. (E16.2.7) can be integrated analytically to yield

$$t = \frac{1}{k(C_{B0} - 2C_{A0})} \ln \frac{C_{B0} - 2C_{A0}f_A}{C_{B0}(1 - f_A)} \quad (\text{E16.2.11})$$

or

$$f_A = \frac{1 - \exp[k(C_{B0} - 2C_{A0})t]}{2C_{A0}/C_{B0} - \exp[k(C_{B0} - 2C_{A0})t]} \quad (\text{E16.2.12})$$

Substituting the parameters, one obtains $f_A = 0.0336$ at $t = 45 \text{ min}$.

At exactly 45 min, the heat of generation as defined by Eq. (E16.2.10) is given by

$$H_G = (-r_A V)(-\Delta H_R) = 3882 \text{ kcal/min}$$

The maximum cooling available for the heat of removal

$$H_{R,\max} = UA_H(T - T_a) \leq 35.85 \times (175 - 25) \text{ kcal/min} = 5377.5 \text{ kcal/min}$$

which is more than sufficient to control the temperature in the reactor. One can conclude that the explosion would not have happened if the cooling was not turned off.

(b) Adiabatic operation for the next 10 minutes

The cooling was turned off from the time of 45–55 minutes. We now solve Eqs. (E16.2.7) and (E16.2.8) with ODEXLims, noting that the initial conditions are

$$t = 45 \text{ min}; f_A = 0.0336; T = 175 + 273.15 \text{ K}$$

and $UA_H = 0$.

At the end of the 55 minutes, the solution is given by $f_A = 0.0430$ and $T = 468.16 \text{ K} = 190^\circ\text{C}$. Correspondingly, $H_G = 6569.4 \text{ kcal/min}$ and $H_{R,\max} = 6094.8 \text{ kcal/min}$. The point of no return has already reached for the reactor is set to fail should it continue to operate. The temperature is going to rise even if maximum cooling is applied from this point on.

(c) Batch operation with heat exchange

Continuing the simulation from part b), but let $UA_H = 35.85 \text{ kcal}/(\text{min} \cdot ^\circ\text{C})$. The reactor conditions at the end of the adiabatic operations become the initial conditions for the batch operation with cooling capacity back online. The initial conditions to be used with the ODEXLims are

$$t = 55 \text{ min}; f_A = 0.043009; T = 468.1589 \text{ K}$$

and $UA_H = 35.85 \text{ kcal}/(\text{min} \cdot ^\circ\text{C})$.

Fig. E16.2.2 shows the simulated temperature profile for the reactor operation. We can observe that the temperature continue to rise. More clearly, from Fig. E16.2.3, by 110 minutes (or 10:45 pm), the reactor temperature had reached 515.49 K or 242.3°C. The temperature began increasing even more rapid after this point. One can observe that 120 min after the batch reactor was started the temperature increases sharply and the reactor explodes at a few minutes before midnight. If the mass and heat capacity of the stirrer and reaction vessel had been included, $\sum n_i C_{Pi}$ term would have increased by about 5% and extended the time until the explosion occur by 15 minutes or so, which would predict the actual time of the explosion occurred at 12:18 am.

When the temperature reached 300°C, a secondary reaction, the decomposition of nitroaniline to noncondensable gases such CO , N_2 and NO_2 , occurs, releasing even more heat. The total energy released was estimated to be $6.8 \times 10^9 \text{ J}$, which is enough energy to lift the entire 2500 Mg building 277 m straight up.

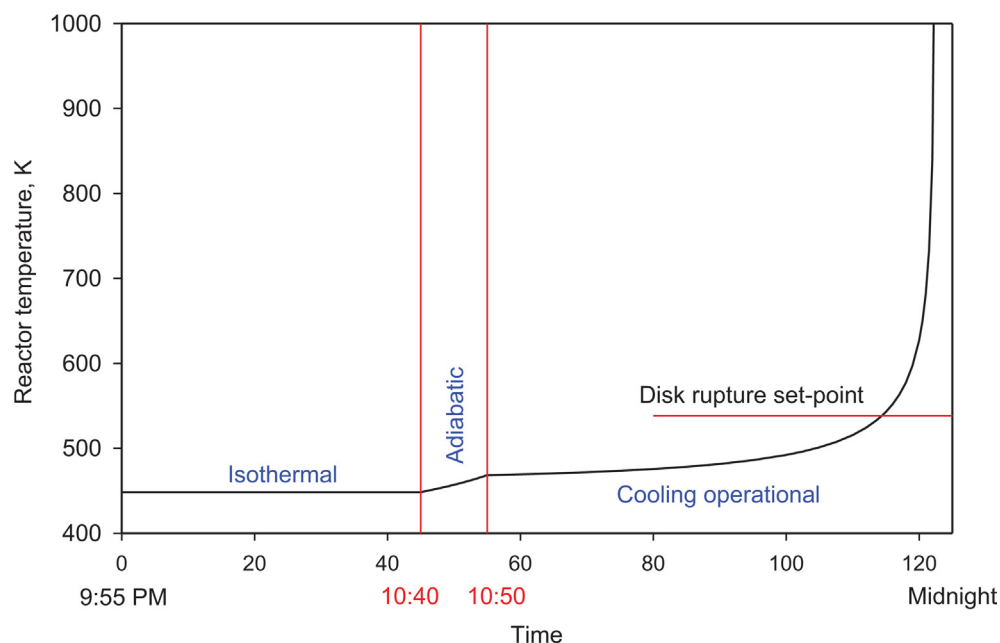


FIGURE E16.2.2 Variation of temperature in the reactor as simulated using ODEXLims. The data sheet is shown in Fig. 16.2.3.

Example-Safety [Compatibility Mod]						
B13 {=ODEXLIMS(A12:A46,B12:C12,,,A3:E3)}						
A	B	C	D	E	F	G
1	C _{A0}	C _{B0}	U _{AH}	V, m ³	ΣnC _P	
2	1.766751	6.446572	0	5.119	2504.9	Adiabatic
3	1.766751	6.446572	35.85	5.119	2504.9	with Heat Exchanger
4						
5	t, min	f _A	T, K	H _R , kcal/min	H _G , kcal/min	k
6	0	0	448.15	0	0	0.00011898
7	45	0.033616	448.15	0	3882.16049	Adiabatic
8	47	0.035136	451.3891	0	4241.04443	
9	49	0.036803	454.9399	0	4665.74415	
10	51	0.038644	458.8622	0	5175.31684	
11	53	0.040697	463.2338	0	5796.74469	
12	55	0.043009	468.1589	6094.8191	6569.44354	
13	57.5	0.046098	468.6488	6112.3822	6620.21463	
14	60	0.049213	469.1741	6131.2152	6676.93346	
15	62.5	0.052356	469.7399	6151.4985	6740.5427	
16	65	0.05553	470.352	6173.4427	6812.16279	
17	67.5	0.05874	471.0173	6197.2939	6893.13377	Heat exchanger on
18	70	0.061991	471.7439	6223.3413	6985.06924	
19	75	0.068637	473.4207	6283.4558	7210.1046	
20	80	0.075526	475.483	6357.387	7509.00398	
21	85	0.082743	478.0769	6450.3809	7915.88281	
22	90	0.090412	481.4242	6570.3807	8487.30888	
23	95	0.098731	485.878	6730.0503	9324.07246	
24	100	0.108029	492.0431	6951.0659	10624.1218	
25	102.5	0.113218	496.0886	7096.1001	11568.5944	
26	105	0.118919	501.0655	7274.5194	12833.9877	
27	107.5	0.125321	507.3352	7499.2887	14599.248	
28	110	0.132728	515.4901	7791.6418	17201.6218	
29	112	0.139724	524.0556	8098.7171	20341.1595	
30	113.5	0.145897	532.2706	8393.223	23780.3334	
31	114.3873	0.15007	538.1504	8604.0133	26520.8037	
32	115	0.153246	542.7904	8770.3586	28858.6274	
33	116	0.159091	551.6798	9089.043	33797.8711	
34	117	0.166047	562.7918	9487.4075	40892.811	
35	118	0.174654	577.2402	10005.385	51816.0877	
36	119	0.185937	597.1482	10719.085	70438.2835	
37	120	0.202181	627.2726	11799.044	107865.747	
38	120.5	0.213838	649.6744	12602.149	144145.785	
39	121	0.23011	681.7133	13750.744	210644.227	
40	121.5	0.255779	733.4815	15606.633	360467.337	
41	122	0.307614	840.4611	19441.852	867962.614	
42	122.5	0.513795	1274.7	35009.309	5250577.78	
43	122.75	0.844184	1973.791	60071.724	6087962.18	
44	123	0.981414	2259.457	70312.867	898181.224	
45	123.25	0.998108	2287.927	71333.513	92475.0659	
46	123.5	0.999807	2284.431	71208.188	9375.91735	

FIGURE E16.2.3 ODEXLims solution of example 16.2.

(d) Disk rupture

The pressure relief disk should have ruptured when the temperature reached 265°C or 538.15 K (ca. 700 psi), but it did not and temperature continued to rise. If it had ruptured, the liquid water would vaporize, a maximum of 10^6 kcal would be able to be drawn from the reaction mixture, thereby lowering the temperature and quenching it.

If the disk had ruptured at 265°C (700 psi), the maximum mass flow rate out of the 2-in orifice to the atmosphere (1 atm) would have been 830 kg/min at the time of rupture. This leads to a maximum heat removal of

$$Q = m\Delta H_{\text{vap}} + UA_r(T - T_a) = 830 \text{ kg/min} \times 540 \text{ kcal/kg} + 35.85 \text{ kcal/K} \times (265 - 25) \\ = 456804 \text{ kcal/min}$$

which is much greater than the heat generation at that time $H_G = 26520.8$ kcal/min. The reaction could have easily been quenched.

16.14 Summary

Chemical transformation and biotransformation are the discussions of this text. Transformation as it defines will result in changes. Any changes have irreversible consequences. Managing the changes can help us, while changes can also be harmful. Therefore, safety is of paramount concern when dealing with transformations. The first line of defense on any potential changes or transformations is containment. Large scale quarantine (or containment) on biohazards has been practiced since ancient times. Various regulations by different governments today are based on containment when unknown organisms are to be introduced. For biosafety, stringent regulation and containment are needed. Bioprocess engineers usually deal with microorganisms in processes. The scales or space are usually “small” and containment is local. Different governments have different rules or regulations. WHO defines four risk groups of biosafety levels. Biosafety levels I and II are basic, meaning having minimum risk to the public and/or personnel handling it. Biosafety levels III and IV require strong containment in place. For bioprocess engineers to be proficient in biosafety practice there are six key knowledge bases as defined by the American Biological Safety Association (ABSA). These areas of proficiency include— (1) Disinfection, decontamination, sterilization; (2) Work practices and procedures; (3) Risk assessment and hazard identification—infectious and recombinant DNA; (4) Regulatory aspects, standards, and guidelines; (5). Equipment operation and certification; and (6) Facility design.

To avoid inappropriate handling as well emergency response to accidents, chemicals need to be properly labeled. Chemicals are labeled following standardized systems. However, different countries and/or agencies have different standards. For example, the Hazardous Materials Identification System (HMIS) is a numerical hazard rating that incorporates the use of labels with color developed by the American Coatings Association as a compliance aid for the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard. OSHA is an agency of the United States Department of Labor. Similarly, the fire diamond, created by the National Fire Protection Association (NFPA) is also a numerical hazard rating. The hazards are generally divided into three main categories: health, flammability, and physical. The labeling is visual and easy to be understood. To avoid confusion and promote trade, United Nations has created a universal identification system, global harmonized system of classification and labeling of chemicals (GHS), beginning in 1992. The GHS label includes the substance name, id, eye-catching pictograms to show the potential dangers, warnings and descriptions on how to handle it. GHS hazard classification also includes three categories: Physical, Health and Environment. As compared with HMIS and NFPA labeling, GHS combined the flammability hazards into physical hazard category while one additional category is added: environmental hazard.

Chemical reactivity hazard is defined as a situation where an uncontrolled chemical reaction could result directly or indirectly in serious harm to people, property, or the equipment. As such, the first come into mind of the reactivity hazards is fire and explosion, which usually involves strong exothermic reactions. To safe guard processes and facility, one needs to first identify the threat, or screening for reactivity hazards. When the “threats” are identified, one can then find the remediation(s) for the particular “threats” by adding barriers or change the design if possible to avoid the “threats.” Bioprocess engineers commonly use a design criterion as minimizing the cost or maximizing the profit. Putting barriers to perceived “threats” or potential failures ultimately will increase the cost and foot-print of the facility.

Chain reaction is one of the potential chemical reactivity hazards. Chain reaction is a very common type of chemical reaction, which chemical engineers need to be able to handle and to be aware of how different a chain reaction can be than an “ordinary” reaction, $A \rightarrow \text{products}$, $r = kC_A$, or its variants. Chain reactions are involved in autooxidation and in combustion and also in polymerization. A chain reaction process is composed of a sequence of reaction steps whose rates can vary by large factors. Some of these reaction steps slow the overall process, and some accelerate it, and some of these slow steps can have alternate paths.

In combustion processes the reaction is also highly exothermic, and, combined with the high effective activation energy of combustion processes, leads to large temperature dependence. The overall reaction products can also vary (partial oxidation versus total oxidation), and this factor must also be considered when dealing with combustion processes.

Because of these factors, chain reactions are inherently unpredictable. Chemical and thermal autocatalysis makes the overall rate not a simple function. Chain reactions can also be very fast so that the reaction may be limited by mass transfer processes.

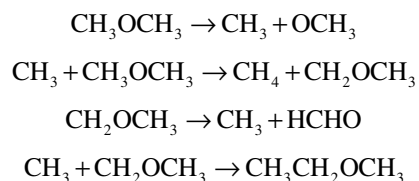
Partial oxidation reactions are important in chemical industry. Pyrolysis and gasification of biomass, for example, are useful technologies in biomass conversion. We frequently do not have reliable reaction rate expressions for chain reactions, but we can compensate for this lack by designing and operating the reactor to manage the overall course of the reaction by properly dealing with mixing, mass transfer, promoters and inhibitors, and the presence of surfaces.

An explosion can be defined as a fast, transient, exothermic reaction. It needs exothermicity to generate energy and must be fast to generate this energy very quickly in a transient pulse. We can also distinguish between events in which the reaction propagates at subsonic velocity as an explosion and one in which the reaction propagates with sonic or supersonic velocity as a detonation. Unintended and accidental explosions can occur due to (1) The accumulation of reactive chemicals (gas, liquid, or solid) in confined space; (2) Leakage of “significant amount” of reactive chemicals (gas, liquid, or solid) to atmosphere or environment; or (3) Reactor runaway. As a bioprocess engineer, you will be responsible for creating safe processes and protecting the lives and health of your colleagues and community.

Problems

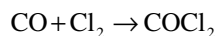
- 16.1** What is biohazard? What is chemical reactivity hazard?
- 16.2** What are the effective methods of combating biohazards?
- 16.3** What are the Biosafety Levels? What are they designed for?
- 16.4** What is reactivity hazard? What are the four typical causes of reactivity incidents?
- 16.5** Develop a model of the burning of a cigarette (from one end of a cylinder). The primary reactions can be regarded as the burning of biomass (59.2wt% C, 8.3 wt% H, 4.5 wt% N and the rest being O) to CO_2 and H_2O in excess O_2 and to CO if oxygen deficient. In the absence of O_2 the tobacco pyrolyzes to carbon with the vaporization of tars and nicotine, which for unexplained reasons some people like to inhale into their lungs.
- What mass- and energy-balance equations are appropriate?
 - What reactions dominate in different regions of the cigarette? Are these reactions homogeneous or heterogeneous?
 - Sketch $C_j(z)$ in the cigarette for O_2 , CO_2 , CO, and tar assuming a steady-state gas velocity and that the length of the cigarette L changes slowly.
 - How does the heat generation and absorption vary with position? Sketch $T(z)$.
 - Illustrate $u(t)$ and $T(z, t)$ during a puff? Sketch $L(t)$.
- Estimate transient temperatures, velocities, and concentrations versus time with as much accuracy as possible.
- 16.6** Model a campfire spark as a spheric wood particle ($\rho = 500 \text{ kg/m}^3$) surrounded by a boundary layer of thickness $2R$ ($Sh = 2$) at 1000°C .
- Summarize in several sentences and equations the model of the combustion of a campfire spark.
 - Why will a small particle be lifted from the fire?
 - One part of this problem is analogous to a hot air balloon. Formulate a model with which you could calculate the size and density for lift and the velocity of the rising spark particle.
- 16.7** Ammonium nitrate (AN) is a common fertilizer that is an excellent source of nitrogen.
- Sketch the flow sheet to manufacture AN from CH_4 , air, and water.
 - Fertilizer bags list three numbers, N, P, and K percentages. What are the NPK ratings of AN and of KNO_3 ?
 - Write a reasonable reaction for the decomposition (explosion) of AN.
 - How does the energy release of AN compare with TNT?
 - How many cubic meters of gas would be produced if 1 cubic meter of AN reacted as above and the products were at atmospheric pressure and 20°C ? At 2000°C ?
- 16.8** A bottle that you thought contained pure diethyl ether actually has autooxidized to 10% diethyl ether hydroperoxide. What is the temperature if the contents of the bottle suddenly react to chemical equilibrium? At what hydroperoxide concentration would the temperature not exceed 100°C ? Assume that the heat of decomposition of the hydroperoxide is 125 kJ/mol .

- 16.9** Dimethyl ether decomposes to methane and formaldehyde. It is assumed that the reaction proceeds according to the elementary steps:

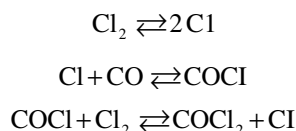


where the first is the initiation step, the second and third are propagation steps, and the fourth is the termination step. Derive a rate expression for this reaction $r = k[\text{CH}_3\text{OCH}_3]^n$ assuming pseudo steady state on radical intermediates.

- 16.10** Phosgene, an intermediate in polyurethane monomer, is made by the homogeneous reaction



The elementary steps of this reaction are



where all reactions are reversible.

- Identify initiation, propagation, and termination steps.
 - Show that the rate of this reaction could be $r = k[\text{CO}][\text{Cl}_2]^{3/2}$
 - Find an expression for the reverse reaction rate.
- 16.11** Consider the combustion of a coal pile of diameter D and height H . Before ignition the air flow is driven by wind, and after ignition by natural convection. The heat of combustion of carbon is -393 kcal/mol. Set up a qualitative energy balance (no numbers) to explain the dependence of combustion on weather and on D and H . What size and shape of coal piles do you recommend to minimize spontaneous combustion?
- 16.12** If a container filled with each of the molecules in Table 16.13 at room temperature and atmospheric pressure suddenly decomposed into C (s) and H_2 , calculate the temperatures and pressures in the container.
- 16.13** A bottle that you thought contained ethanol had oxidized to 10% ethylhydroperoxide. If the contents of this bottle suddenly went to chemical equilibrium, estimate the temperature and pressure in the bottle (for a short time). The heat of formation of ethylhydroperoxide is -172 kJ/mol and the heat of carbon oxidation to CO_2 is -280 kJ/mol.
- 16.14** A 50- μm drop of diesel fuel is injected into the cylinder of an engine with air at 1500°C. Assume dodecane, $D_{\text{O}_2} = 0.01\text{cm}^2/\text{s}$, $P = 10\text{ atm}$, $\rho = 900\text{ kg/m}^3$.
- Estimate the time it would take for complete combustion of the drop. Use the shrinking sphere models of Chapter 16 and assume that the process is limited by O_2 diffusion to the drop surface.
 - Suppose the engine designers require complete combustion in $2 \times 10^{-3}\text{ s}$. What drop size must the fuel injectors produce using the above model?
 - Formulate a more detailed model of liquid drop combustion which includes a homogeneous reaction and the vapor pressure and boiling point of the fuel.
- 16.15** There are several possible ways to make 1,2-propanediol. Illustrate the chemical reactions for each of them and indicate possible advantages and disadvantages of each.
- methylacetylene + H_2O ,
 - propylene + HOCl ,
 - propylene + HOOH ,
 - propylene + ethylbenzene hydroperoxide,
 - propylene + O_2 .

16.16 If a reactor filled with switchgrass powders at room temperature and atmospheric pressure having a bulk density of 200 kg/m^3 , and it suddenly burned into CO_2 (g) and H_2O (g), calculate the temperatures and pressures in the reactor. Determine the minimum amount of oxygen needed in the reactor.

16.17 An excerpt from The Morning News, Wilmington, Delaware (August 3, 1977) shows: “Investigators sift through the debris from blast in quest for the cause [that destroyed the new nitrous oxide plant]. A company spokesman said it appears more likely that the [fatal] blast was caused by another gas – ammonium nitrate – used to produce nitrous oxide”. An 83% (wt) ammonium nitrate and 17% water solution is fed at 200°F to the CSTR operated at a temperature of about 510°F . Molten ammonium nitrate decomposes directly to produce gaseous nitrous oxide and steam. It is believed that pressure fluctuations were observed in the system and as a result the molten ammonium nitrate feed to the reactor may have been shut off approximately 4 min prior to the explosion.

- Can you explain the cause of the blast? [Hint: examining the potential temperature change through energy balance]
- If the feed rate to the reactor just before shutoff was 310 lb of solution per hour, what was the exact temperature in the reactor just prior to shut down?
- How would you start up or shut down and control such a reactor?

Assume that at the time the feed to the CSTR stopped, there was 500 lb of ammonium nitrate in the reactor at a temperature of 510°F . The conversion in the reactor is virtually complete at about 99.99%. Additional information: $\Delta H_R^\circ = -336 \text{ Btu/lb-ammonium nitrate at } 500^\circ\text{F}$; $C_p = 0.38 \text{ Btu/(lb-ammonium nitrate}\cdot^\circ\text{F)}$; $C_p = 0.47 \text{ Btu/(lb-steam}\cdot^\circ\text{F)}$ and $r = k C_A$, with $k = 0.53 \text{ h}^{-1}$ at 510°F and $k = 5.03 \text{ h}^{-1}$ at 560°F . The enthalpies of water and steam are: $H_L (200^\circ\text{F}) = 168 \text{ Btu/lb}$ and $H_G (500^\circ\text{F}) = 1202 \text{ Btu/lb}$.

16.18 Explore the ONCB explosion described in Example 16.2. Show that no explosion would have occurred if the cooling was shut off for 10 min after 9.04 kmol charge of ONCB or if the cooling was shut off for 10 min after 45 min of operation for the 3.17 kmol ONCB charge. Show that if the cooling had been shut off for 10 min after 12 h of operation, no explosion would have occurred for the 9.04 kmol charge. Develop a set of guidelines as to when the reaction should be quenched should the cooling fail. Perhaps safe operation could be discussed using a plot of the time after the reaction began at which the cooling failed, t_0 , versus the length of the cooling failure period, t_f , for the different charges of ONCB. Parameter values used in this example predict that the reactor will explode at midnight. What parameter values would predict that the reactor would explode at the actual time of 18 min after midnight? Find a set of parameter values that would cause the explosion to occur at exactly 12:18 am. For example, include heat capacities of metal reactor and/or make a new estimate of UA_H . Finally, what if a 1/2-in rupture disk rated at 800 psi had been installed and did indeed rupture at 800 psi (270°C)? The explosion still would have occurred. (Note: The mass flow rate varies with the cross-sectional area of the disk. Consequently, for the conditions of the reaction the maximum mass flow rate out of the 1/2-in disk can be found by comparing it with the mass flow rate of 830 lb/min of the 2-in disk.

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